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LIQUID CRYSTAL MATERIALS

FOR MATRIX DISPLAYS

J. David Margerum and Anna M. Lackner

Hughes Research Laboratories
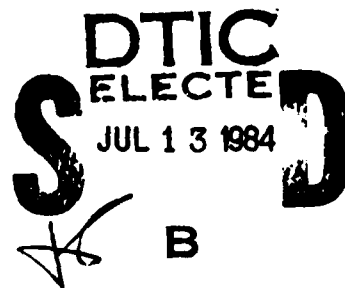3011 Malibu Canyon Road
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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Studies are made on several basic areas relating to the properties and behavior of liquid crystal (LC) mixtures for use in dynamic scattering (DS) electro-optical applications, particularly in dc-activated matrix displays at elevated temperatures. These studies include the analysis of the major factors affecting DS characteristics, the development of methods to formulate new LC mixtures with desirable predicted properties for DS displays, investigations of structural effects on the viscosity of LC components of negative dielectric anisotropy, and examination of the dc-DS properties and lifetime of improved LC mixtures used at elevated temperatures. New LC eutectic mixtures with wide nematic ranges are shown to be operable in the 20 to $71^\circ C$ range, with good storage stability in the -60 to $80^\circ C$. The feasibility is shown for long dc-DS lifetime at elevated temperatures (75000 hr at $55^\circ C$ with 20 Vdc) in well-sealed cells. Recommendations are made for further studies on dc-DS in thin cells with pulsed signals, and for improvements in the yield of well-sealed cells. $80 \, ^\circ C.$ $71 \, ^\circ C$

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SECTION 1

INTRODUCTION AND SUMMARY

A. INTRODUCTION

These studies are a continuation of investigations[1,2,3]
on "Liquid Crystal Materials for Matrix Displays" under ONR
Contract Numbers N00014-79-C-0524 and N00014-81-C-0307. The
overall goal of this program is to develop liquid crystal (LC)
materials and techniques suitable for use in MOSFET matrix
displays being developed by Hughes Aircraft Company for several
military applications, including an integrated head-up airplane
cockpit display, a helmet-mounted display, a color alphanumeric
display, a flat panel status advisory display, and a missile
sighting system. (MOSFET refers to the metal oxide semi-
conductor field effect transistors which are used as switches in
the circuitry for each picture element in the silicon substrate
of the LC matrix display. A bibliography of related Hughes
publications in this area is shown in Section 6.) The key LC
material problems are related to requirements that such military
displays must be storable over a wide temperature range (about
-60 to 80°C) and must be operable in ambient temperature ranges
between about -50° and 71°C. Because it is much easier to heat
LC displays then to cool them, and also because fast response
times (up to TV rate) are needed, our program is aimed
especially at the use of LCs in the upper part of the
operational range. Thus, our goal is to have displays that are
operable up to 71° from ambient heating, and that are heated to
a minimum cell temperature (probably in the 25 to 40°C range)
when the ambient conditions are not warm enough.

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The LC electro-optical technique that has been used in the Hughes matrix display is the dc-activated dynamic-scattering (DS) mode. The dc-DS has advantages over ac activation in permitting the use of simpler substrate circuitry, in operation at lower voltages, and in providing a good gray scale range. Redox dopants are us_d to ester LCs to give efficient scattering at relatively low voltages, and to permit long operational lifetime capability in the dc mode at room temperature. These dopants provide adequate conductivity and conductivity anisotropy for dynamic scattering, and they also protect the LC by carrying essentially all of the current through the cell by means of the electrochemical reversibility of their oxidation and reduction reactions.

The research problems regarding the LC materials for the dc-DS matrix displays are centered on improving their properties (nematic temperature range, viscosity, dielectric anisotropy, conductivity anisotropy, etc.) and on maintaining the integrity of the redox dopant and of functioning sealed cells over a wide range of temperatures. The sealant material must not contaminate the LC with impurities that significantly alter its conductivitly, DS efficiency, electrochemical stability, and surface alignment. The thermal stability of the LC must be optimized for both storage and operational lifetime at elevated temperatures. The LC response times must be optimized for high contrast, TV rate pictures over a wide range of elevated temperatures when updated at 30 times/sec. The LC must have high dc-DS efficiency at lower operating temperatures (higher LC resistivity), as well as at higher temperatures (lower resistivity), and the ratio of decay-time/on-time must be optimized to widen the operational temperatures range. Other key problem areas of study are the stability of the LC surface alignment at low storage temperatures and at high operating temperatures.

B. SUMMARY OF RESULTS

The research studies in the prior ONR contracts were directed toward evaluating the applicability of LC materials and cells for dc-DS at elevated temperatures, as related to the MOSFET matrix displays. Those results are summarized in the final reports[1,3] and in a technical publications.[2] The research studies of the present contract were directed toward several key areas of basic concern related to the properties and behavior of LC mixtures for DS effects and for use in matrix displays. These studies included the analysis of the major factors affecting DS characteristics, the development of methods to formulate new LC mixtures with desirable predicted properties for DS displays, investigations of structural effects on the viscosity of LC components of negative dielectric anisotropy, and examination of the dc-DS properties and lifetime of improved LC mixtures used at elevated temepratures. These research studies are presented in the following four publications (which are included in full in the Appendixes):

- "Factors Affecting the Anisotropic and Dynamic Scattering Characteristics of an Ester Mixture," by J. David Margerum, Anna M. Lackner, Hong S. Lim, and John E. Jensen

- "Formulation and Predicted Properties of Nematic Eutectic Mixtures of Esters," by J.D. Margerum, A.M. Lackner, J.E. Jensen, L.J. Miller, W.H. Smith, Jr., S.-M. Wong, and C.I. van Ast.

- "Effects of Cyclohexyl Groups and Ortho-Substituents on the Viscosity of Ester Liquid Crystal Components," by J.D. Margerum, S.-M. Wong, J.E. Jensen, C.I. van Ast, and A.M. Lackner.

- Improved Materials for dc Dynamic Scattering at Elevated Temperatuares," by A.M. Lackner and J.D. Margerum.

C.   SUMMARY OF STATUS AND RECOMMENDATIONS

Significant progress has been made in evaluating the factors affecting DS, in correlating structural effects on flow viscosity of LCs, in formulating and predicting properties of new multicomponent LC ester eutectic mixtures with wide nematic ranges, in obtaining long term storage stability of new LC mixtures, and in demonstrating the fessibility of long lifetime dc-DS operation of sealed cells at elevated temperature

Limitations are observed particularly in the dc-DS efficiency and response times in thin cells (where the response time should be fast) at elevated temperature, in the correlation of low viscosity with fast response times, and in the yield of well-sealed cells for long dc-DS lifetime at high temperture. Recommendations are made for additional studies to address these limitations, to determine their mechanisms, and to evaluate the response of LC cells to shaped repetitive pulse signals such as would be generated across the LC in a MOSFET matrix display operated at elevated temperatures. The dc-DS limitations in the cells are believed to be due primarily to space-charge effects, and the lifetime limitations are probably due to contanination of LCs by sealant material still containing some residual uncured components even after ultraviolet exposure of the optical cement.

SECTION 2

RESEARCH RESULTS

A. FACTORS AFFECTING THE ANISOTROPIC AND DYNAMIC SCATTERING
    CHARACTERISTICS OF AN ESTER MIXTURE

1. Abstract

Various factors affecting the anisotropic and dynamic
scattering (DS) characteristics of a 3-component eutectic mixture
of phenyl benzoates are investigated in detail. The effects of
dopant, surface alignment, signal, cell thickness, and
temperature are studied. Different dopant structures give
conductivity anisotropy values in the 1.01 to 1.60 range and this
has the largest effect on the DS threshold voltage at room
temperature. However, cell thickness also changed the threshold
slightly and has a large effect on the magnitude of the
scattering obtained above threshold. Thinner cells give higher
DS levels, higher multiplexing capabilities, and greater off-
angle scattering. The optical density of scattering increases
linearly with the reciprocal of cell thickness. At elevated
temperatures the conductivity anisotropy, viscosity and elastic
constant values all decrease. However, with the increasing
temperature the DS threshold voltage decreases, indicating that
changes in viscosity and elastic constants with temperature are
more significant than the decrease in conductivity anisotropy.

2. Introduction

We are interested in using the dynamic scattering mode in
liquid crystal (LC) devices such as pictorial matrix displays,
reticle devices, and automobile dashboard displays. Phenyl
benzoate ester mixtures of negative dielectric anisotropy are of

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interest for DS, because they are colorless, can be purified
adequately for controlled doping, show good dc stability when
used with redox dopants, and have relatively good thermal
stability at elevated temperatures. In many of these
applications it is desirable to have a low threshold voltage
(V_{th}) for the DS mode. The present study is designed to
evaluate, in detail, the factors affecting the V_{th} and
scattering levels of a phenyl benzoate LC mixture. These factors
include the conductivity dopant, resistivity, temperature,
surface alignment, applied signal and cell thickness. A simple
LC eutectic mixture (HRL-2N25) containing just three phenyl
benzoate components is used for these studies, and its properties
are also characterized as a function of temperature.

3. <u>Conclusions</u>

   In brief, our studies with this phenyl benzoate LC mixture
show the following correlations:

- The V_{th} for DS is strongly affected by the choice
   of conductivity dopant, LC surface alignment, and the
   applied voltage frequency. The effect of dopant
   conductivity anisotropy on V_{th} is well correlated
   over $\succ$ wide range by Helfrich's equations for both
   su⌐ ,-parallel and surface-perpendicular LC alignment
   at   ac frequencies. A similar trend is observed
   wiᴛₙ dc signals, but the correlation is obscured by
   electrochemical effects. In general, the lowest
   V_{th} values are obtained with high conductivity
   anisotropy, surface-parallel alignment, and dc
   signals.

- In this LC the V_{th} is also affected by the LC
   resistivity, cell thickness, and temperature. Smaller
   ac-V_{th} values are obtained with lower resis-
   tivity, with a cell thickness of about 25 μm, and at
   higher temperatures up to about 50°C. At these
   elevated temperatures the V_{th} is less affected by
   the decrease in conductivity anisotropy than by the
   offsetting decreases in the elastic constant and
   viscosity of the LC.

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- When compared at an applied voltage of 2 x V_{th}, thinner cells show higher scattering levels, higher multiplexing capability and more off-angle scattering than thicker cells. Both the "optical density" of scattering and the maximum multiplexing capability increase linearily with the reciprocal of the cell thickness.

B.   FORMULATION AND PREDICTED PROPERTIES OF NEMATIC EUTECTIC MIXTURES OF ESTERS

1.   Abstract

Techniques are described both for formulating new nematic liquid crystal eutectic mixtures and for calculating several of their predicted properties. Ester LC components from various structure classes are used. Emphasis is placed on obtaining mixtures which have relatively short average molecular length, and which are suitable for dynamic scattering electro-optical applications. Examples are given of binary eutectic mixtures made with LC esters of essentially the same molecular length. Selection rules are described for mixing short length components, both from homologous series and from different classes of esters. Approximate class values of birefringence, dielectric anisotropy, and viscosity are assigned to each type of ester structure, based on experimental results in selected mixtures of short molecular length. Properties of multi-component eutectic mixtures are ca_culated, and comparisons are shown between the predicted and the observed values of melting point, clearpoint, viscosity, dielectric anisotropy, and birefringence of new ester mixtures developed for dynamic scattering devices and displays.

2.   Introduction

Multicomponent liquid crystal mixtures are generally needed to obtain a nematic phase with a wide temperature range. In the formulation of LCs for dynamic scattering applications, we have shown that it is advantageous to use short molecular length components to obtain low viscosity and other favorable

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properties. However, special selection techniques are required in choosing components in order to prepare LC eutectic mixtures when combining short length ester components of similar molecular length. Otherwise, such components can act as solid solutions and not give a lowered melting point. It is also highly desirable to be able to predict key anisotropic properties as well as the nematic temperature range of each new multicomponent mixture being considered for use. In this paper both of these issues are addressed. We describe selection rules for obtaining binary eutectic mixtures with ester components of essentially equal molecular length, and we show how to use these LC pairs in the formulation of multicomponent eutectic mixtures with relatively short molecular length. We also show how we assign approximate class values of birefringence (Δn), dielectric anisotropy ($\Delta\varepsilon$), and viscosity (η) to the various types of ester structures being considered for use in our mixtures. Finally, we compare actual experimental values versus our predicted calculations of nematic melting point (mp) and clearpoint (clpt.), as well as predicted values of Δn, $\Delta\varepsilon$, and η at 25°C for several multicomponent LC ester mixtures of interest for dynamic scattering applications.

3. Conclusions

Multicomponent ester eutectic mixtures with short average molecular length can be prepared by including selected binary, tertiary, and quaternary sets of short length ester LC components of essentially equal molecular length. Two methods are found to be suitable for selecting eutectic LC binary sets (and combinations thereof to give tertiary and quaternary sets) with equal length components. Guidelines are described for combining these binary sets together with other components, and such multicomponent ester eutectics are each found to have a nematic temperature range close to the theoretical one calculated by applying the Schroeder-Van Laar equation.

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Approximate class values of birefringence and dielectric anisotropy (as well as viscosity, reported elsewhere) can be assigned by measuring the effect of specific class components on these properties in a standard short length RO-R' mixture. These class values are found to be useful in several ways. Their relative magnitude provides a basis for qualitative comparisons of structural effects on these anisotropies. The assigned class values are also very useful in predicting, with fairly good accuracy, the room temperature values of Δn, $\Delta \epsilon$, and η for new multicomponent ester mixtures.

Several new short length, multicomponent, eutectic mixtures of ester LCs are successfully formulated with the properties desired for dynamic scattering applications. These new mixtures have a wide nematic range, relatively low viscosity, slightly negative dielectric anisotropy, and good compatibility with redox dopants for dc-activation.

C. EFFECTS OF CYCLOHEXYL GROUPS AND ORTHO-SUBSTITUENTS ON THE VISCOSITY OF ESTER LIQUID CRYSTAL COMPONENTS

1. Abstract

Structural effects on the relative viscosity of liquid crystal ester components are studied by capillary flow viscosity measurements of each component as an additive (10 to 25%) in a standard nematic mixture of short length 4-alkoxyphenyl 4-alkylbenzoates. An approximate class viscosity at 25°C is calculated and assigned to each additive component, indicative of its viscosity contribution in the environment of the phenyl benzoate mixture. Studies are made on the viscosity effects of replacing benzene rings with cyclohexane rings, and of using various ortho-substituents on phenyl groups. All of the additive components are esters or thioesters, including several newly synthesized compounds. The effect of a cyclohexyl group is strongly dependent on its position in the structure. The class viscosity values show a large decrease when

cyclohexanecarboxylate replaces benzoate, only a modest decrease when cyclohexylbenzoate replaces biphenylcarboxylate, and a slight increase when a cyclohexyl ester replaces a phenyl ester. Although o-groups can be used effectively to alter the dielectric anisotropy and modify the nematic range of a component, they increase the class viscosity values substantially, with the magnitude of the viscosity effect in the following approximate order from several o-groups: $Br > CN > CH_3 > pyridyl > Cl$.
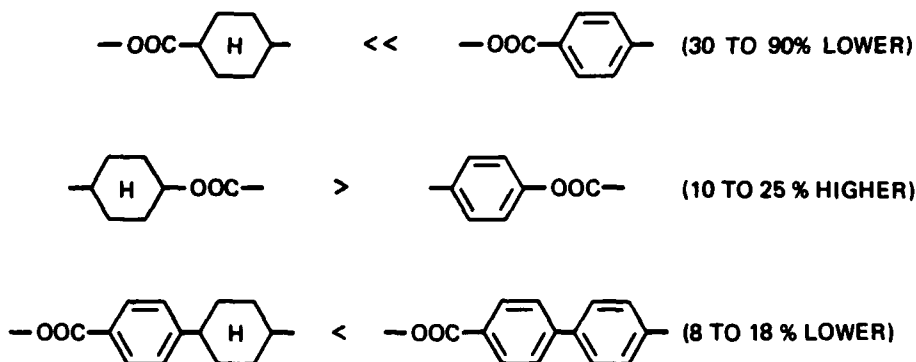
2.   Introduction

The effects of chemical structure on liquid crystal viscosity are important considerations in the selection of a component for nematic mixtures used in display applications. For example, it is desirable to be able to predict the viscosity of a new multicomponent LC mixture accurately enough to decide whether or not it is worthwhile to make up a calculated eutectic mixture for study. We have previously described the assignment of approximate class viscosity values (n_{class}) to eighteen different classes of ester LC structures, and we have shown that these n_{class} values are useful in predicting the viscosity of new mixtures. We are particularly interested in developing additional new LC mixtures with low viscosity, negative dielectric anisotropy, and wide nematic temperature range for both dynamic scattering and field-effect display applications. In working toward these goals, we report here more detailed studies on the viscosity effect of structural changes in LC esters in which phenyl groups are replaced by cyclohexyl groups, or in which o-substituents are used on phenyl groups. Twenty additional ester structures are assigned n_{class} values, and systematic comparisons are made on the changes in class viscosities with structural variations.

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3. Conclusions

The replacement of phenyl rings by cyclohexyl rings in ester LC compounds alters their relative value of class viscosity, with the magnitude and the direction of the effect strongly dependent upon the position of the cyclohexyl groups in the structure. When the class viscosities are extrapolated from viscosity measurements of the LC compounds as additives in a standard host mixture of alkoxyphenyl alkylbenzoates, then for otherwise comparable structures the effects on η_{class} of replacing a phenyl ring with a cyclohexyl ring are typically as follows:

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$$-OOC\text{—}\boxed{H}\text{—} \quad << \quad -OOC\text{—}\bigcirc\text{—} \quad \text{(30 TO 90\% LOWER)}$$

$$-\boxed{H}\text{—}OOC\text{—} \quad > \quad -\bigcirc\text{—}OOC\text{—} \quad \text{(10 TO 25 \% HIGHER)}$$

$$-OOC\text{—}\bigcirc\text{—}\boxed{H}\text{—} \quad < \quad -OOC\text{—}\bigcirc\text{—}\bigcirc\text{—} \quad \text{(8 TO 18 \% LOWER)}$$

Thus, substitution of a cyclohexyl for a phenyl ring adjacent to the carbonyl group is by far the most effective way of using cyclohexyl rings to reduce the viscosity of ester LC structure.

Although o-groups can be used effectively to control the dielectric anisotropy contribution of component structures, and also to lower the melting point, this advantage is offset by a substantial increase in the class viscosity of a structure with

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an o-group as compared to the structure without it. In the present studies the presence of an o-group in a component increases the n_{class} value in the range of 20 to 200%. For these structures the magnitude of the o-group effect on n_{class} increases as follows:
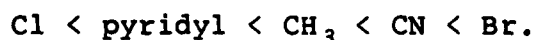
$$Cl < pyridyl < CH_3 < CN < Br.$$

The assignment of class viscosities to LC ester structures is useful in comparing structural effects of cyclohexyl rings and o-substituents on the relative viscosity contributions of ester and thioester LC compounds. The twenty n_{class} values assigned here along with the other eighteen assigned earlier, can be used effectively to predict the flow viscosity of new multicomponent LC nematic mixtures.

D. IMPROVED MATERIALS FOR DC DYNAMIC SCATTERING AT ELEVATED TEMPERATURES

1. Abstract

Liquid crystal mixtures and a sealant suitable for dc-activated dynamic scattering matrix displays are developed for wide range storage temperature (-60 to 80°C) and for elevated temperature operation. Three improved eutectic nematic mixtures are formulated with nematic ranges (undoped) of 0 to 74, -4 to 82, and -13 to 78°C, with flow viscosities of 31, 32 and 36 cP respectively. Several types of sealants are tested in contact with LC and are evaluated according to the level of contamination they introduce at elevated temperature. One UV-curved sealant shows no apparent degradation effects after more than 1800 hours of 100°C heating with an undoped ester LC in a vacuum-filled test cell made with this sealant. Thermal storage stability at 80°C and low temperature stability at -60°C in such sealed cells show little change in surface alignment,

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resistivity, and DS characteristics in LCs with redox dopants, namely dialkylferrocene and (2,4,7-trinitro-9-fluorenylidene)-malononitrile. The LC materials with this redox dopant also show good thermal stability for over 1100 hours at 100°C in evacuated glass ampoules. Elevated temperature dc-DS stability with 20 V dc at 55°C shows more than 5000 hours for two of the new redox-doped LC mixtures in sealed transparent cells. The viscosity, dielectric anisotropy, conductivity anisotropy, and dc-activated DS effects are studied as a function of temperature for one of the mixtures. Response times of DS as a function of temperature (25° to 65°C) and cell thickness are also studied.

2.   Introduction

The dynamic scattering mode is useful for several types of liquid crystal display applications, most of which require a wide temperature range for device storage as well as a fairly wide operational temperature range for the LC materials. However, because the DS mode is dependent upon the anisotropic conduction of ionic species, the operational range is in general somewhat limited due to the exponential dependence of ionic conduction upon temperature. We are particularly interested in using dc-activated DS for an active-matrix pictorial LC display with MOS (metal-oxide-semiconductor) substrate circuitry. The dc-DS mode provides a gray scale capability for this matrix display, and dc-activation of the LC picture elements (pixels) is the simplest way to utilize the MOS circuitry. In this circuitry a field effect transistor (FET) is switched open just long enough to charge a pixel capacitor, which provides the activating voltage across the LC pixel during each picture frame time (e.g., 33 ms). The LC must be conductive enough to give a full level dc-DS response, but must be resistive enough so that the capacitor remains sufficiently charged to maintain an adequate voltage across the LC during the frame time. At room temperature with a typical LC thickness (e.g., 10 μm) the operational range for the

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LC resistivity in this MOSFET addressed display is approximately between 10^9 and 10^{10} ohm-cm. The resistivity is strongly temperature dependent for redox doped LC esters, with an order of magnitude change between about 25 and 70°C for the ac-resistivity and between about 35 and 71°C for the apparent dc-resistivity for cells activated at 20V.

Although the use of redox dopants permits long lifetimes for the dc-activation of ester LCs, the resistivity of unsealed cells gradually increases over long periods of dc operation, even in nitrogen-flushed ovens. On the other hand, cells sealed with epoxy type sealants have shown a very short dc-lifetime at elevated temperatures due to electrochemical effects from ionic impurities introduced into the LC from the sealant material. The present work was initiated with the goal of obtaining improved LCs and sealants compatible with the dc-activation of MOS-addressed matrix displays in the elevated temperature range of about 35 to 71°C. Cells can be readily heated, and operation above room temperature is advantageous for faster response times. In addition, environmental conditions may require operation up to about 71°C in some cases if the cells are not cooled. Our aims were (1) to develop improved redox-doped ester LC mixtures with a wider nematic temperature range, lower viscosity, and faster response times, and (2) to obtain sealants compatible with these LCs and capable of permitting long life dc-activation of MOS-addressed matrix cells at elevated temperatures as well as long term storage at both high and low temperatures.

3. Conclusions

Of three new LC ester eutectic mixtures with lower viscosity which were formulated for DS applications, HRL-26N36 is superior to HRL-26N25 and -26N35 in the width of its nematic range (-13° to 78°C, undoped) and in its scattering level for dc-DS with redox dopants added.

Thinner cells show faster dc-DS response times than thicker cells, although with less change than the usual square of thickness relationship. However, thin cells show decreased scattering levels at high temperatures and high voltages (e.g.,> 50°C and >15 V). This may be due to space charge build up at the PVA-coated electrodes caused by the higher current levels.

At elevated temperatures the scattering vs voltage curve peaks at intermediate voltages (e.g., 10 to 12 V), and the ratio of decay-time/on-time increases. These effects and the fast on-times at the higher temperatures could compensate for a shorter length pulse, such as might occur in a MOSFET matrix display if the charge on the pixel capacitor leaks appreciably during a frame time due to the higher conductivity of the LC at high temperatures.

An optical cement, Norland NOA-61, was found to be superior to many other sealants (especially epoxy types) in its thermal stability with ester LCs at elevated temperatures. Well sealed cells showed that long term dc-DS stability is possible at elevated temperatures (e.g., >6000h at 55°C and 20 V dc). However, the lack of reproducibility in fabricating well sealed cells was found to be the limiting factor in the yield of long live dc-DS test cells.

The new mixtures with redox dopants show favorable long term storage stability in sealed cells between low and high temperatures of -60° to 80°C.

SECTION 3

STATUS AND RECOMMENDATIONS

A. STATUS

1. Factors Affecting Dynamic Scattering.

The effects of LC anisotropic properties, dopants,
temperature, and cell parameters have been correlated with DS
characteristics. Although many of these correlations are
similar for both ac-DS and dc-DS, there are several distinct
differences which appear to be related to the elecrochemical
reactivity of the dopant/LC mixture and to space charge
effects. One of the significent differences is that in thin
cells the dc-DS efficiency drops off at high voltages (espe-
cially at elevated temperatures) whereas the ac-DS is more
efficient in thin cells. The response times of dc-DS appear to
be strongly dependent upon the length and repetition rate of the
activating pulses, especially in thin cells. We believe that
space charge effects probably limit the efficiency and response
times of dc-DS in thin cells at elevated tempratures, although
these effects are not yet well understood.

2. LC Structure Effects on Viscosity.

The effects of a wide variety of LC ester component
structures on viscosity are now well documented, and the flow
viscosity of multicomponent LC mixtures can be predicted with
good accuracy. However, the dc-DS response times in cells with
surface-parallel alignment are not consistently shortened by use
of lower viscosity LC mixtures, indicating that other factors
(elastic constants, etc.) probably also have significant effects
on the response times.

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3. Formulation of LC Mixtures with Predicted Properties

Multicomponent LC mixtures have been formulated successfully with observed values of their nematic range, birefringence, dielectric anisotropy, and viscosity close to the predicted values calculated. Formulation techniques have been especially devised for eutectic ester mixtures with short average molecular length and low viscosity. However, the efficiency of dc-DS (e.g. voltage required for 90% scattering) is not yet fully optimized as a function of structure and anisotropic properties.

4. Storage Stability of LC Mixtures at High and Low Temperatures.

New multicomponent ester LC mixtures with "redox" dopants have shown good storage and alignment stability in cells betweeen -60° and + 80°C.

5. Long dc-Activated Lifetime at Elevated Temperatures

The feasibility of obtaining long lifetime dc-DS operation at elevated temperature has been demonstrated with new LC mixtures in well sealed cells, using an improved sealant material. However, the yield of fabricating long-lifetime cells is not high, apparently due to lack of reproducability in the curing of this optical cement. Also, the mechanisms causing lifetime limitations are not yet understood.

B.   RECOMMENDATIONS

1.   Study Causes for Low Efficiency dc-DS in Thin Cells at Elevated Temperatures

Evaluate effects of surface alignment layer, LC composition (especially dielectric anisotropy), and conductivity dopants on the dc scattering efficiency as a function f elevated temperature and cell thickness. Determine the mechanism for the fall-off of scattering efficieny, and the formation of domains in thin cells. Seek improved scattering levels and response times in thin cells for dc-DS.

2.   Study LC Response to Pulsed Signals Simulating Those in a MOSFET Matrix Display

Study the effect of pulse length and repetition rate on the dc-DS characteristics. Evaluate the dc-DS response to pulse shapes at TV rates typical of those generated by MOSFET matrix substrate circuitry across LCs at elevated temperature.

3.   Study Cell Surface Effects on LCs and dc-DS

Evaluate the extent of dopant absorption on cell surfaces and how this is affected by temperature and dc activation conditions. Determine the effect of LC surface alignment layers on dopant absorption and on "chromatogaphy" effects in the filling of cells.

4.   Study Sealants and Sealing Techniques

Seek improved reproducibility for high quality (non-contaminating) curing with optical cements. Evaluate humidity effects on dc-DS lifetimes of sealed cells at various temperatures. Optimize choice of sealant and sealing technique for high yields of well-sealed, long-life cells for dc-DS at elevated temperature.

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SECTION 4

RESEARCH PERSONNEL

The following research personnel participated in these studies.

Dr. J. David Margerum, Senior Scientist....Principal Investigator
Mrs. Anna M. Lackner, Member Technical Staff....Project Leader
Dr. Siu-May Wong, Consultant
Dr. John E. Jensen, Member Technical Staff
Mrs. Camille I. van Ast, Development Engineer Senior

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SECTION 5

PRESENTATIONS AND PUBLICATIONS

1. J. David Margerum, Anna M. Lackner, Hong S. Lim, and John E. Jensen, "Factors Affecting the Anisotropic and Dynamic Scattering Characteristics of an Ester Mixture," presented at the Fifth International Symposium on Liquid Crystals and Ordered Fluids, American Chemical Society Meeting, St. Louis, MO, April 9-13, 1984. (Liq. Cryst. and Ordered Fluids, Vol. 5, Gordon & Breach, N.Y., in press.)

2. J.D. Margerum, A.M. Lackner, J.E. Jensen, L.J. Miller, W.H. Smith, Jr., S.-M. Wong, and C.I. Van Ast, "Formulation and Predicted Properties of Nematic Eutectic Mixtures of Esters," presented at the Fifth International Symposium on Liquid Crystals and Ordered Fluids, American Chemical Society Meeting, St. Louis, MO, April 8-13, 1984. (Liq. Cryst. and Ordered Fluids, Vol. 5, Gordon & Breach, N.Y., in press.)

3. J.D. Margerum, S.-M. Wong, J.E. Jensen, C.I. Van Ast, and A.M. Lackner, "Effects of Cyclohexyl Groups and Ortho-Substituents on the Viscosity of Ester Liquid Crystal Components," presented at the Tenth International Liquid Crystal Conference, York, U.K., July 15-21, 1984.

4. Anna M. Lackner and J. David Margerum, "Improved Materials for DC Dynamic Scattering at Elevated Temperatures," presented at the Tenth International Liquid Crystal Conference, York, U.K., July 15-21, 1984.

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SECTION 6

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APPENDIX A

FACTORS AFFECTING THE ANISOTROPIC AND
DYNAMIC SCATTERING CHARACTERISTICS OF AN
ESTER MIXTURE*

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Various factors affecting the anisotropic
and dynamic scattering (DS) characteristics
of a 3-component eutectic mixture of phenyl
benzoates are investigated in detail. The
effects of dopant, surface alignment,
signal, cell thickness, and temperature are
studied. Different dopant structures give
conductivity anisotropy values in the 1.01
to 1.60 range and this has the largest
effect on the DS threshold voltage at room
temperature. However, cell thickness also
changed the threshold slightly and has a
large effect on the magnitude of the
scattering obtained above threshold.
Thinner cells give higher DS levels, higher
multiplexing capabilities, and greater off-
angle scattering. The optical density of
scattering increases linearly with the
reciprocal of cell thickness. At elevated
temperatures the conductivity anisotropy,
viscosity and elastic constant values all
decrease. However, with the increasing
temperature the DS threshold voltage
decreases, indicating that changes in
viscosity and elastic constants with
temperature are more significant than the
decrease in conductivity anisotropy.

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1. INTRODUCTION

We are interested in using the dynamic
scattering (DS) mode[1] in liquid crystal (LC)
devices such as pictorial matrix displays[2,3,4],
reticle devices[5,6], and automobile dashboard
displays[7]. Phenyl benzoate ester mixtures of
negative dielectric anisotropy are of interest
for DS, because they are colorless, can be
purified adequately for controlled doping[8], show
good dc stability when used with redox
dopants[9,10] and have relatively good thermal
stability at elevated temperatures[11]. In many
of these applications it is desirable to have a
low threshold voltage (V_{th}) for the DS mode.
The present study is designed to evaluate, in
detail, the factors affecting the V_{th} and
scattering levels of a phenyl benzoate LC
mixture. These factors include the conductivity
dopant, resistivity, temperature, surface
alignment, applied signal and cell thickness. A
simple LC eutectic mixture (HRL-2N25) containing
just three phenyl benzoate components is used
for these studies, and its properties are also
characterized as a function of temperature.

2. EXPERIMENTAL

Most of the experimental techniques employed
here have been described[11,12]. The ester LC
components are synthesized and purified by
standard methods. Liquid chromatography

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analysis indicates that these components have
less than 0.1% impurity. The room temperature
resistivity of the undoped LC mixture is greater
than 10^{11} ohm-cm, typically about 4×10^{11}
ohm-cm. The dopants are prepared in the
following ways: Tetracyanoethylene (TCNE) from
Aldrich is recrystallized from methylene
chloride and then sublimed at 70°C.
Tetrabutylammonium trifluoromethanesulfonate
(TBATMS) is prepared as previously reported[8].
Ethylpyridinium tetraphenylboride (EPTPB) and
tetrabutylammonium tetraphenylboride (TBATPB)
are prepared in the manner described by Mann[13],
with recrystallization from acetone/water
solutions before drying. Dibutylferrocene (DBF)
from Research Organic Chem. is distilled at
115°C at 0.3mm. (2,4,7 Trinitrofluorenylidene)-
malononitrile (TFM) from Aldrich is
recrystallized from acetonitrile.
(2,4,5,7-Tetranitrofluorenylidene)malononitrile
(T4FM) is synthesized by reacting 2,4,5,7-
tetranitro-9-fluorenone with malononitrile; the
reactants are from Aldrich, and the product is
recrystallized from acetonitrile. Dodecyl-
(ethyl)dimethylammonium p-hexyloxybenzoate
(ZLI-235) is used as obtained from E. Merck.

The DS is measured[8] in transmission at
normal incidence and the V_{th} is obtained by
extrapolation back to the baseline of no
scattering, using unpolarized green light
centered at 525nm. In the scattering angle

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measurements the light is incident normal to the cells, and the detector system is rotated off-normal. With no DS the light intensity reaching the detector is 1% of normal transmission intensity at $\pm 4.5°$. Several different surface alignment techniques are used. Cells with surface-parallel LC alignment are made by rubbing ITO (indium tin oxide) electrode surfaces, or by rubbing a thin coating of polyvinyl alcohol (PVA) on ITO after drying in an oven, or by shallow angle ion beam etching of ITO, or by medium angle deposition (MAD) of SiO on ITO[14]. The surface-perpendicular LC alignment is made by bonding a long chain alcohol $(C_{18}H_{37}OH)$ onto a thin (150Å) coating of MAD-SiO on ITO, except in the field effect measurements (no DS) where the C_{18} alcohol treatment is used on a SiO_2 (800 Å) coating in order to minimize the tilt angle[15]. Cell thickness variations are made using various Mylar films as perimeter spacers for normal thickness. The actual thickness of the thinner LC cells is calculated from the resistance measurements of each cell and the resistivity of each LC sample in thicker cells (50.8 or 127 µm). The width of the Williams domains[16] is measured with a Zeiss Standard WL polarizing microscope, using minimum applied voltages in the range of 1.04 to 1.23 times V_{th}.

FACTORS AFFECTING DYNAMIC SCATTERING

3. RESULTS AND DISCUSSION

3.1 LC Eutectic Mixture

A three component eutectic ester mixture,
identified as HRL-2N25, is formulated using
p-ethoxyphenyl p-propylbenzoate (20-3),
p-hexyloxyphenyl p-butylbenzoate (60-4),
and p-hexyloxyphenyl p-methoxybenzoate (60-01)
as shown in Table I. The ratio of components is
calculated with the Schroeder-van Laar equation.
The actual nematic range, observed by
differential scanning calorimetry, has both a
lower melting point and clearpoint than the
calculated values. Several other properties of
the mixture are also summarized in Table I,
including the average molecular length (L)
which is determined from measurements of
molecular models in the extended
configuration[12]. The dielectric anisotropy ($\Delta\epsilon$)
is more negative than mixtures of 100% RO-R'
(e.g 20-3, 60-4, etc.) components[12] due to the
RO-OR' (60-01) component. The capillary flow
viscosity (η) is relatively high due to the
medium size L and the presence of 60-01 as
shown by other studies of RO-R'/RO-OR'
mixtures[17]. The viscosity data fit the
expression $\eta = A \exp(E_\eta/RT)$ quite well.

3.2 Dopants and Conductivity Anisotropy

Purified mixtures are usually not conductive and
will show DS effects only if ionic species are

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Table I. HRL-2N25 Eutectic Mixture

Component Code	L (Å)	mp (°C)	Clpt. (°C)	ΔH_f kcal/mole	Mole Fraction
20-3	19.67	76	68	6.72	.132
60-4	25.78	29	48	4.20	.640
60-01	23.60	55	80	6.19	.228

Properties

Calc. nematic range: 13° to 57°C

Obs. nematic range: 0° to 54°C

Av. molecular length: $\bar{L}$ = 24.48 Å

Dielectric anisotropy: $\Delta\varepsilon$ = -0.39 (24°C, 1kHz)

Birefringence: Δn = 0.14 (23°, 589nm)

Freedericks transition: V_{FT} = 7.0 V (23°C)

Density: d = 1.059 g/ml (25°C)

Flow viscosity: η = 48.5 cP (25°C)

Viscosity activation energy: E_η = 9.3 kcal/mole

present or are generated by the applied field. Both the ionic conductivity and its anisotropy depend upon the structure of dopant as well as the LC[8,18,19]. The seven dopants in this study are chosen to provide a wide range of conductivity anisotropy ($\sigma_\parallel/\sigma_\perp$) values. In this ester mixture the $\sigma_\parallel/\sigma_\perp$ of each dopant except TBATMS is nearly independent of concentration, as indicated in Figure 1. Except for EPTPB and T4FM, these dopants have been studied in various other LCs and similar results are found here. In HRL-2N25 at 25°C the $\sigma_\parallel/\sigma_\perp$ value is 4 to 6% higher for TBATMS, TBATPB, and DBF/TFM than in

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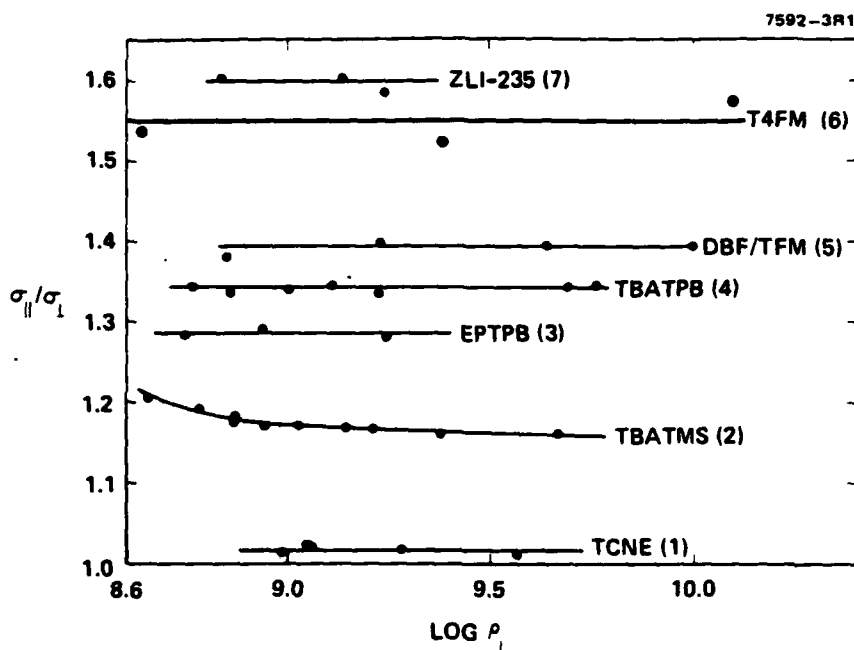
FIGURE 1 Conductivity anisotropy of dopants
in HRL-2N25 at 23°C as a function
of resistivity ($\rho_\perp$ at 100 Hz).

the HRL-2N10 ester mixture[8], is 5% lower for
ZLI-235 than in a Schiff base-ester mixture[20],
and is 3% lower than TCNE in an azoxy LC[21].
Although changes in the dopant structure often
have a larger effect on the conductivity
anisotropy of nematic mixtures than changes in
the LC structure, much larger variations of $\sigma_\parallel/\sigma_\perp$
are observed in other LC mixtures in which
cybotactic nematic characteristics are
present[11,12,22].

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3.3. Effects of Dopant, Alignment, and Frequency on V_{th}

Figure 2 shows plots of V_{th} for ac-DS (30 Hz for both surface-perpendicular and surface-parallel cells) and for dc-DS (surface-parallel), each as a function of the conductivity anisotropy of the seven dopants in HRL-2N25. The dopants are identified by the number indicated in Figure 1. In these samples the DS cutoff frequency is greater than 250 Hz, so that approximately cons-stant V_{th} values are observed for dopants 2-7 in the 10-30 Hz range. In dopant 1 (TCNE) the value of V_{th} is progressively lower in going from 30 Hz to 20 Hz and to 10 Hz, indicating that in this case some electrochemical reactions are lowering the V_{th} value at the low frequencies. The conductivity anisotropy has a very large effect on V_{th} in both types of surface alignments and with dc-DS as well as ac-DS. (The dc-DS measurements are less reproducible, but typical V_{th} values are shown here. The relatively high dc-V_{th} for dopant 7 may be due partly to its strong tendency to cause surface-$\perp$ alignment). For a given dopant the DS thresholds here follow the pattern: ac-$V_{th}(\perp)$ > ac-$V_{th}(\parallel)$ > dc-$V_{th}(\parallel)$. This supports earlier observations discussed regarding other LC/dopant systems[23]. Charge injection effects[10] appear to play a dominant role in the dc-activated cells. In contrast to ac-activation, the microscopic patterns of the instability under dc-activation vary with the

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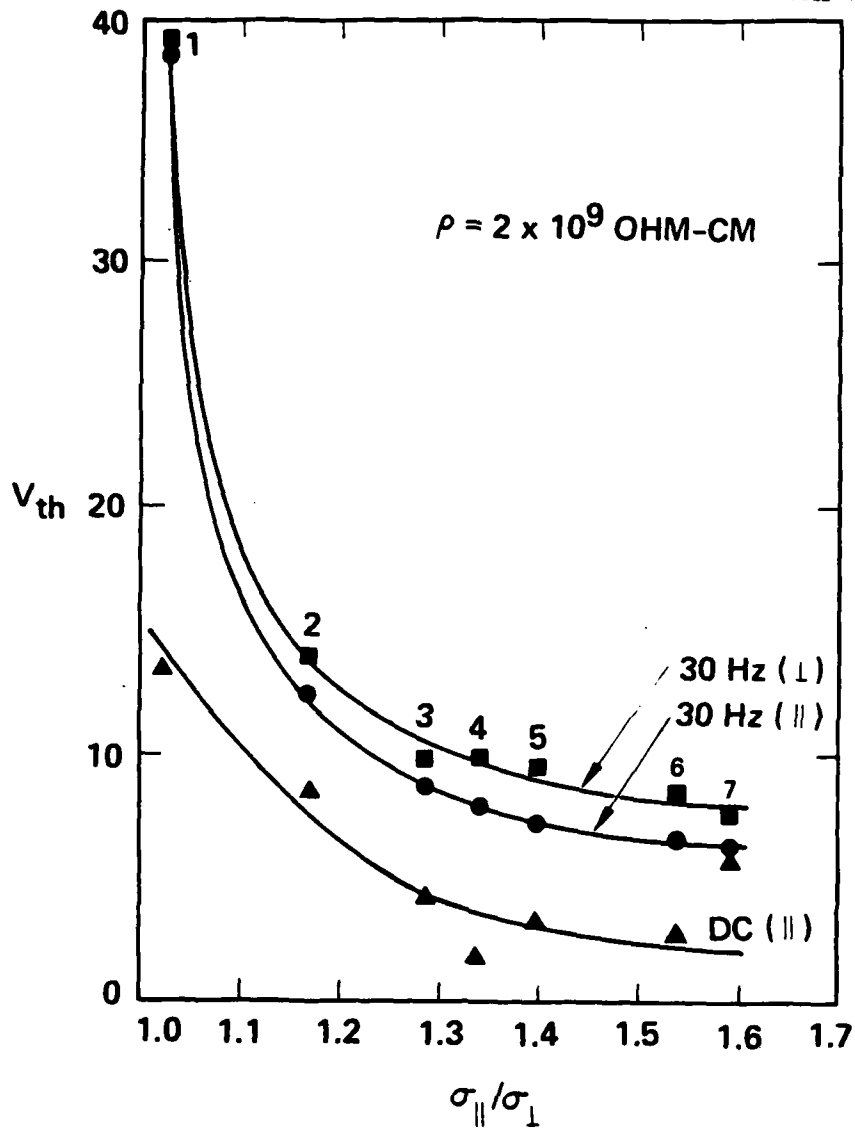
FIGURE 2   Dynamic scattering threshold
voltage as a function of the con-
ductivity anisotropy and surface
alignment of HRL-2N25 containing
the dopants in Table 1.   (23°C,
$\rho_\perp = 2 \times 10^9$ Ω-cm, ■-surface-$\perp$,
● and ▲-surface-$\parallel$).

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individual dopants. The general appearance of
these patterns are similar to a wallpaper
pattern while the ac-activated Williams domains
consist of many parallel line domains. The dc-
V_{th} decreases with increasing $\sigma_\parallel/\sigma_\perp$, but the
values do not fit the correlation derived by
Helfrich[24] for the Williams domain threshold
variation with $\sigma_\parallel/\sigma_\perp$, even though the expression
was derived for dc fields. It should be noted
that the values of conductivity anisotropy are
obtained with ac measurements at 100 Hz. This
gives the $\sigma_\parallel/\sigma_\perp$ for the ionic species present in
the bulk of the LC from the dopant under
equilibrium conditions. It does not measure the
conductivity anisotropy of electrochemically
generated ionic species which are formed by dc
activation, and such ions could have a larger
anisotropy than the initial dopants. This is
the case for T4FM, whose V_{th} values (both ac and
dc) decrease after periods of dc-activation. If
the ionic transport in the dc cells is carried
by both dopant ions and dc-generated ions of
higher conductivity anisotropy, then this could
explain the observed dc results.

The qualitative expressions derived by
Helfrich[24] for the V_{th} of Williams domains
(corresponding here to the ac-V_{th} of DS)
indicate that the correlations shown in
equations 1 and 2 should be followed if small
amounts of conductivity dopants in HRL-2N25
change only its $\sigma_\parallel/\sigma_\perp$, and do not affect the

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values of A, B, C and D.

- Surface-∥ :
$$V_{th}^{-2} = A \left(\frac{\sigma_{\|}}{\sigma_{\perp}}\right)^{-1} + B \quad , \tag{1}$$

where, $A = \dfrac{1}{4\pi^3 k_{33}} \left(\Delta\epsilon - \dfrac{K_1 \epsilon_{\|}}{\eta_1}\right)$; $\quad B = \dfrac{K_1 \epsilon_{\perp}}{4\pi^3 k_{33} \eta_1}$

- Surface-⊥ :
$$V_{th}^{-2} = C \left(\frac{\sigma_{\|}}{\sigma_{\perp}}\right) + D \quad , \tag{2}$$

where, $C = \dfrac{-1}{4\pi^3 k_{11}} \left(\Delta\epsilon + \dfrac{K_2 \epsilon_{\perp}}{\eta_2}\right)$; $\quad D = \dfrac{K_2 \epsilon_{\|}}{4\pi^3 k_{11} \eta_2}$

The expressions of V_{th} with ac activation[25,26] contain extra terms of frequency dependence. However, these terms drop out if the frequency applied is substantially below the cut-off frequency, which is the case in the present studies. Using the ac data from Figure 2, there is a good fit of the surface-parallel data with Equation 1, and of the surface-perpendicular data with Equation 2, as shown by the least-square plots in Figure 3. These results indicate that in each of these surface alignment boundary conditions the effects of various dopants on the ac-V_{th} is determined largely by the conductivity anisotropy of the dopant in the LC.

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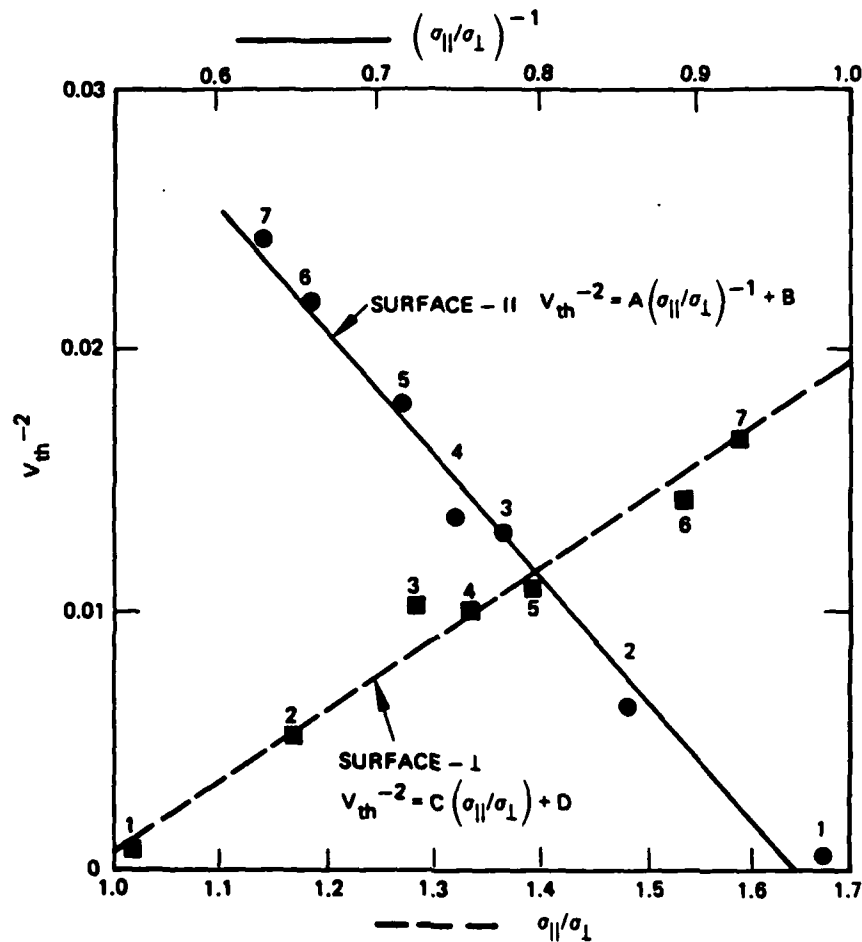
FIGURE 3 Helfrich equation plots for sur-
face-dependence of ac dynamic
scattering V_{th} on $\sigma_{\parallel}/\sigma_{\perp}$

3.4 Effects of Resistivity on V_{th}

Some effects of LC resistivity (ρ) on the ac and
dc values of V_{th} are shown in Figure 4 for
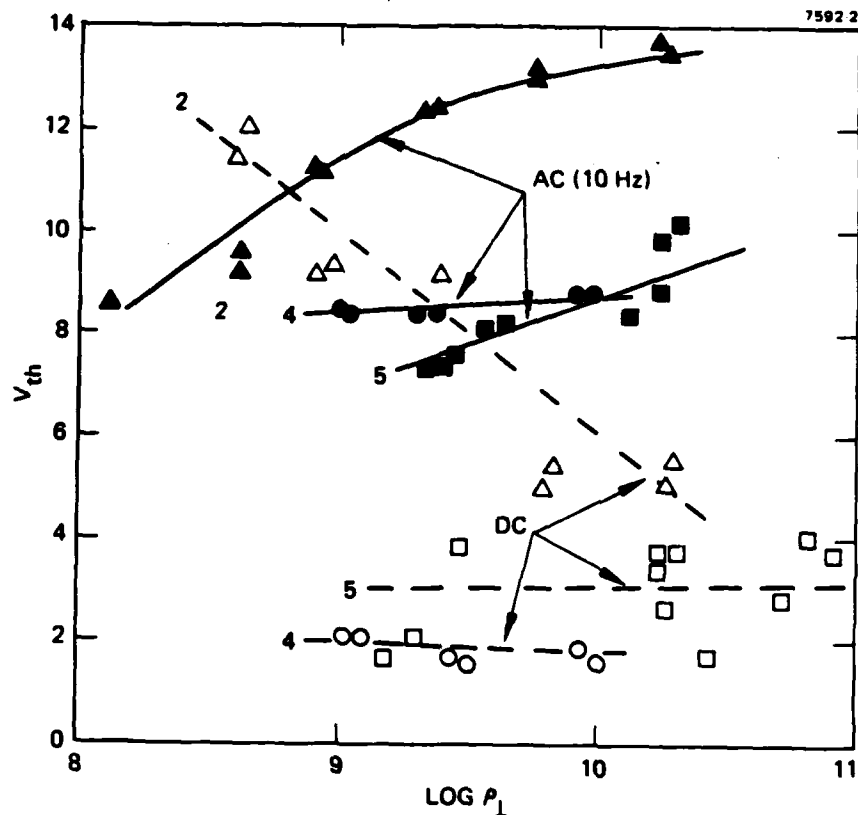
FIGURE 4   Effect of resistivity ($\rho_\perp$ at 100 Hz)
on dynamic scattering V_{th} of doped
HRL-2N25 in 12.7 μm thick cells
with surface-‖ alignment, rubbed ITO.

O, ● - TBATPB (4); Δ, ▲ - TBATMS (2);
□, ■ - DBF/TFM (5).

dopants 2, 4, and 5.   In each case the ac-V_{th}
increases as ρ increases.   In the TBATMS
samples, the change in ac-V_{th} is partially
accounted for by the changes of its conductivity
anisotropy with ρ, which are shown in Figure 1.
However, since the $\sigma_\parallel/\sigma_\perp$ values of TBATPB and

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DBF/TFM are constant with ρ some other (unknown) factor causes their V_{th} to change with ρ. The dc-V_{th} effects vary with the electrochemical properties of the dopants. The dc-V_{th} of TBATMS-doped samples decreases markedly as ρ increases. This dopant is more electrochemically stable than the LC, and the LC probably reacts under a dc field to give LC^+ and LC^- species[9,10] which may have relatively high conductivity anisotropy. At a ρ of 10^9 ohm-cm the LC contains about 10^{-4}M TBATMS, giving an ionic concentration of approximately 10^{-5}M. As the ionic concentration is decreased, the concentration of the positive ions in the vicinity of the positive electrode and of the negative ions in the vicinity of the negative electrode will be decreased as a result of coulombic interaction. Thus dc generated LC ions would be expected to contribute to the ionic transport current, and this becomes more significant as ρ is increased. The ρ of the TBATMS-doped cells under continuous dc-DS decreases significantly only after hours of activation[9], presumably due to irreversible reactions of the LC^+ and LC^- species. On the other hand, the ρ of TBATPB-doped samples changes fairly rapidly (in 10 minutes) with dc-activation, indicating that the dopant itself reacts readily and irreversibly at the electrodes. These reactions of TBATPB appear to result in species of high $\sigma_\parallel/\sigma_\perp$, giving low dc-

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V_{th} values for the short lifetime period of the
samples. The DBF/TFM dopant pair is a redox
system chosen to protect the LC by reacting
readily and reversibly at the electrodes[9,10].
For a ρ of 10^9 ohm-cm the neutral DBF and TFM
compounds are each added in about 3×10^{-2}M, so
that there are larger concentrations of these
redox dopants present than in the case with the
salt dopants. Because of their electrochemical
stability and the amounts of DBF and TFM
present, the dc-V_{th} is relatively stable for
very long periods of dc activation. The
variations of dc-V_{th} for DBF/TFM in Figure 4 may
be due to some differences in the surface
adsorption of these dopants on the electrodes.

3.5 Effects of Cell Thickness

The ac-V_{th} of DS is not constant with the thick-
ness of the cell, as shown by the upper plot in
Figure 5. There is a V_{th} minimum at thicknesses
of approximately 25 µm. In thicker cells the
V_{th} increases appreciably, possibly due to the
increase in the ℓ/λ term as shown by equation 3
and the lower curve in Figure 5 (where ℓ is the

$$V_{th} = \pi \left(\frac{2\ell}{\lambda}\right) \left[\frac{k_{33}/\epsilon_0}{\frac{\kappa_{\perp}\epsilon_{\parallel}}{\eta_1}\left(\frac{\epsilon_{\perp}}{\epsilon_{\parallel}} - \frac{1}{R_\sigma}\right) + \frac{\Delta\epsilon}{R_\sigma}}\right]^{1/2} \qquad (3)$$

cell thickness and λ is the Williams domain
periodicity). However, in cells thinner than
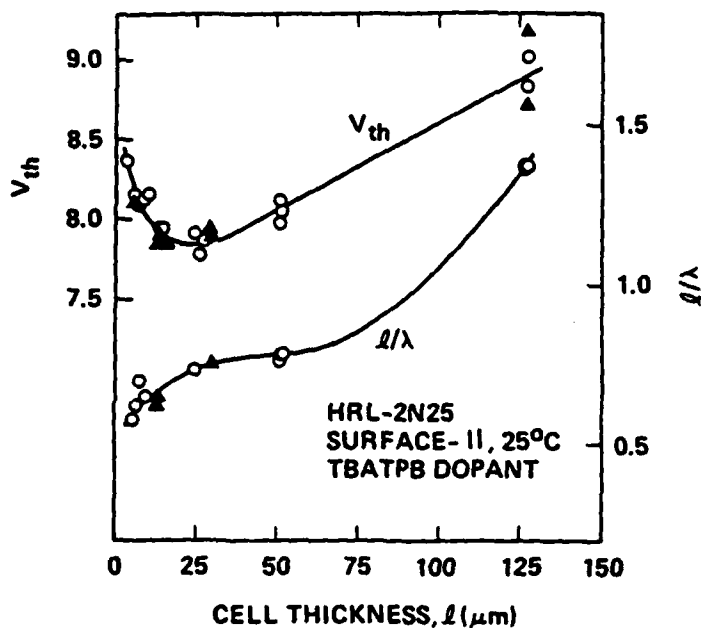
FIGURE 5 Effect of cell thickness on DS-V_{th}
and on domain periodicity (λ), 30Hz.
○ rubbed PVA on ITO
▲ rubbed ITO, or ion-beam etched ITO

25 μm the V_{th} also increases while the l/λ term
decreases. We do not know the reason for the
increased V_{th} in thin cells. Cells with and
without PVA coatings for surface-‖ alignment
gave the same results, so the effect does not
appear to be an artifact related to a voltage
drop across the PVA. Also the resistivity
changes have little effect in the range used
with ρ between 6.15 x 10^8 and 1.36 x 10^9 ohm-cm.

The scattering level of DS (where
% S = 100 - % T, for cells measured in
transmission with light at normal incidence) is

52
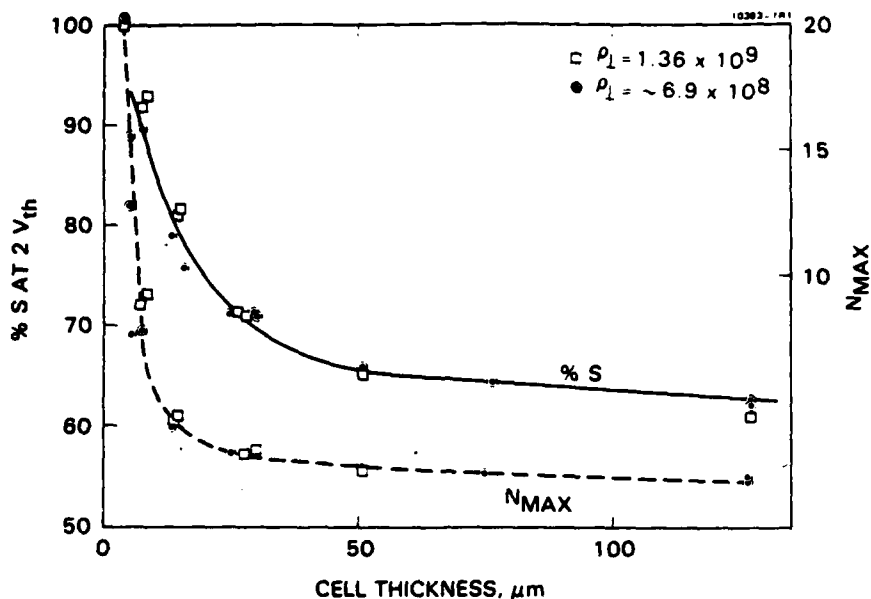
FIGURE 6   The effect of cell thickness on %S
and on N_{max} at 70%S (23°C).

higher in thinner cells. This is shown in
Figure 6, where the % S is plotted versus cell
thickness at 2 x V_{th} for each thickness. The %
S increases sharply in thin cells (we did not
use cells thin enough to observe the expected
decrease in very thin cells). We find a linear
relationship between the optical density of
scattering and the reciprocal of the cell
thickness as shown in Figure 7. In Figures 6
and 7 the maximum multiplexing capability[27]
(N_{max}) for 70% S is also shown. The N_{max}
increases greatly in thin cells, which of course
also have the advantages of having much faster
response times.
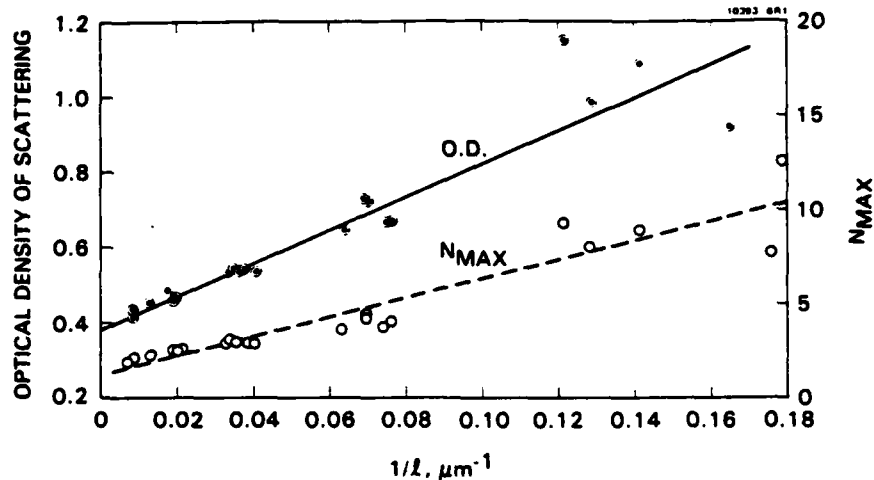
FIGURE 7   Reciprocal length plots for the optical
density of scattering (-log T) and the
maximum multiplex capability.

The data in Figures 6 and 7 are from
measurements made with normal incident light
scattered by DS at relatively small off-angles
(about ± 4°). The effect of cell thickness on
light scattered at larger off-angles is also
examined. As shown in Figure 8, the intensity
of off-angle scattered light in the 4-15° range
is higher for a thin cell than for thicker
cells. (Here the relative intensities are given
as the values measured at 2 x V_{th} divided by the
intensity at that angle from a one-half
Lambertian plate.) Thus, the results from
Figure 8 indicate that the DS efficiency of thin
cells is superior to that of thick cells for
light scattered at larger (4-15°) angles as well
as at small angles.

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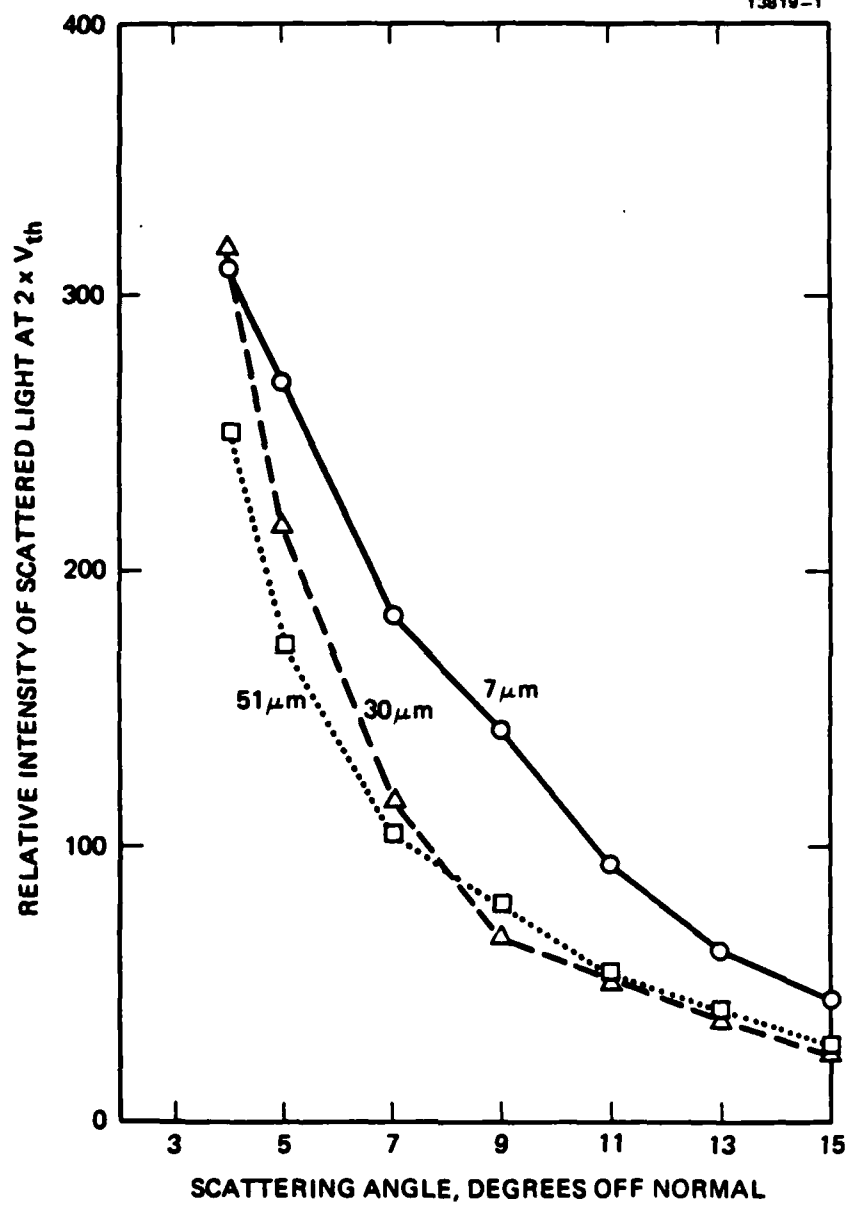
FIGURE 8   Cell thickness effect on off-angle DS
intensity.

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3.6 Temperature Effects

The effects of temperature on several anisotropic and electro-optical properties of HRL-2N25 are shown in Figures 9 and 10. The Freedericks transition in Figure 9 refers to the field effect threshold in a surface-$\perp$ cell. The values of $(V_{th}{}')_{FT}$ and $\Delta\varepsilon$ in Figure 9 are used to calculate the k_{33} elastic constant shown in Figure 10. The $\sigma_{\parallel}/\sigma_{\perp}$ and V_{th} values of DS are measured using TBATPB as a conductivity dopant. The most interesting result in Figure 10 is that the DS-V_{th} values decrease with increasing temperature (at least up to 50°C) while the $\sigma_{\parallel}/\sigma_{\perp}$ also decrease in the same temperature range. This is surprising considering the large effect that $\sigma_{\parallel}/\sigma_{\perp}$ has on the V_{th} (see Figure 2). It indicates that the temperature effects on other parameters such as elastic constants and viscosity coefficients are large enough and in the opposite direction, to offset the decrease of $\sigma_{\parallel}/\sigma_{\perp}$. This is consistant with the large decreases observed in k_{33} and η with increasing temperature.

4. CONCLUSIONS

In brief, our studies with this phenyl benzoate LC mixture show the following correlations:

    1. The V_{th} for DS is strongly affected by the choice of conductivity dopant, LC surface alignment, and the applied voltage frequency.
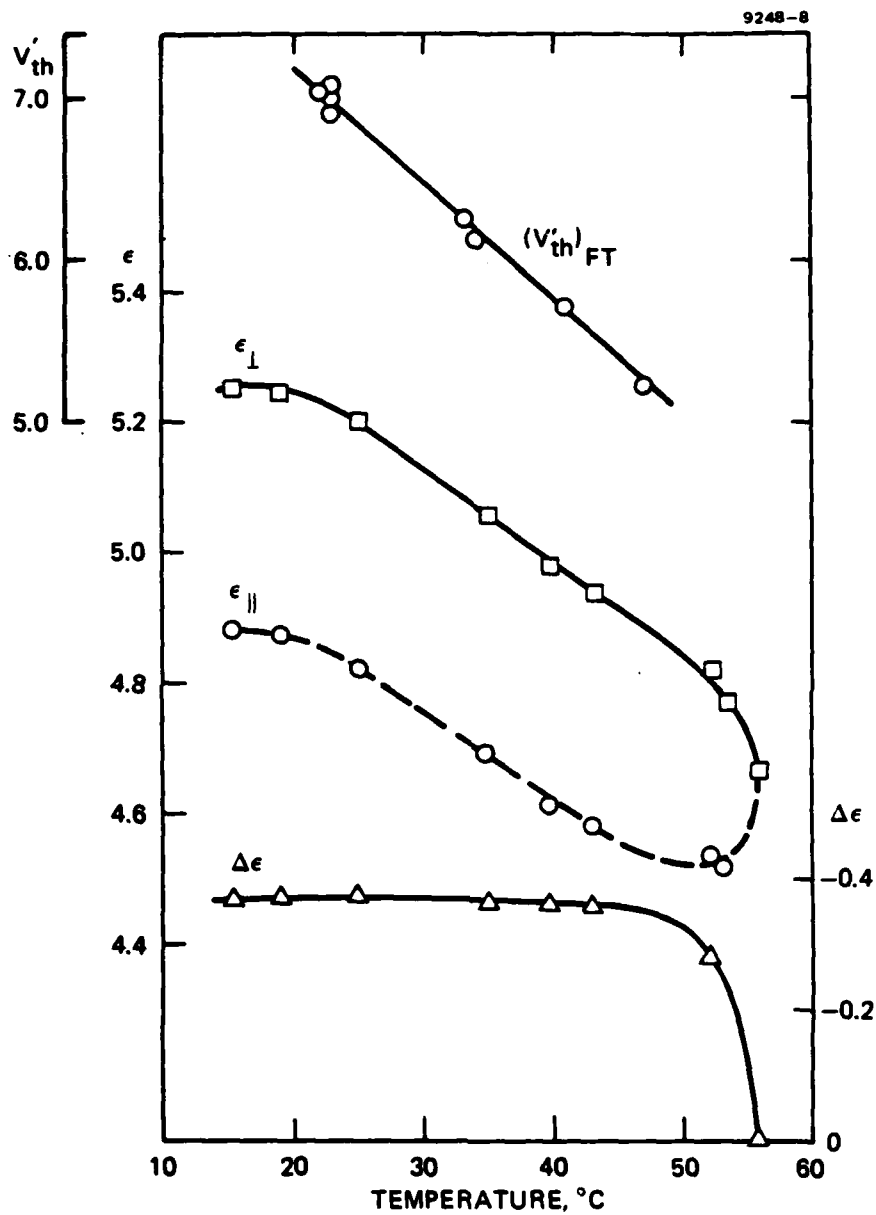
FIGURE 9   Temperature effects on dielectric pro-
perties and Freedericks transition of
HRL-2N25 (undoped).

9899-5
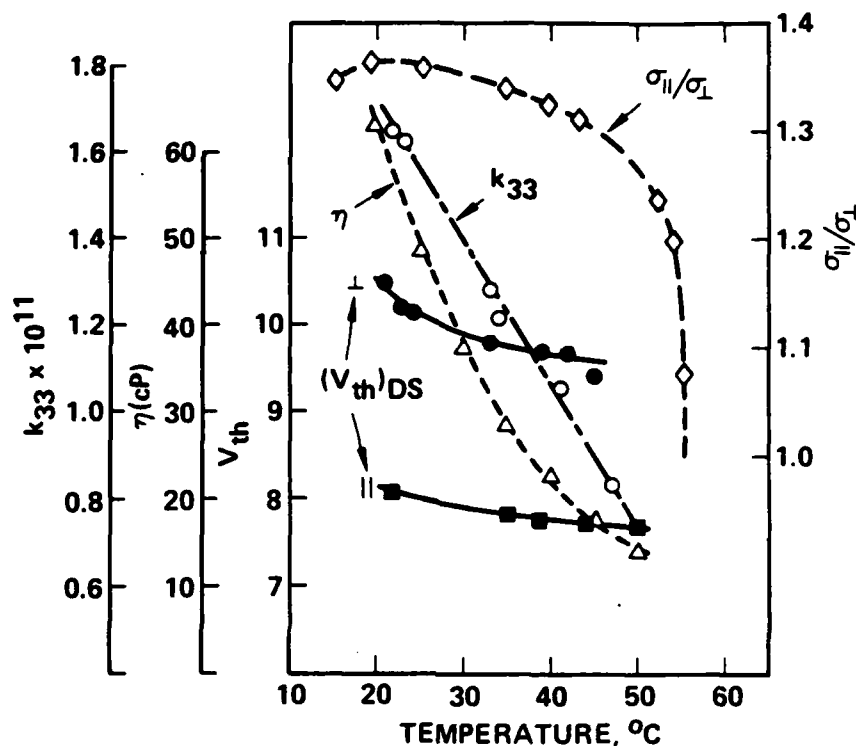
FIGURE 10 Temperature effects on properties of
HRL-2N25, with TBATPB dopant.

The effect of dopant conductivity anisotropy on
V_{th} is well correlated over a wide range by
Helfrich's equations for both surface-parallel
and surface-perpendicular LC alignment at low ac
frequencies. A similar trend is observed with
dc signals, but the correlation is obscured by
electrochemical effects. In general, the lowest
V_{th} values are obtained with high conductivity
anisotropy, surface-parallel alignment, and dc
signals.

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FACTORS AFFECTING DYNAMIC SCATTERING

   2.   In this LC the V_{th} is also affected by
the LC resistivity, cell thickness, and
temperature. Smaller ac-V_{th} values are obtained
with lower resistivity, with a cell thickness of
about 25 μm, and at higher temperatures up to
about 50°C. At these elevated temperatures the
V_{th} is less affected by the decrease in
conductivity anisotropy than by the offsetting
decreases in the elastic constant and viscosity
of the LC.

   3.   When compared at an applied voltage of
$2 \times V_{th}$, thinner cells show higher scattering
levels, higher multiplexing capability and more
off-angle scattering than thicker cells. Both
the "optical density" of scattering and the
maximum multiplexing capability increase
linearly with the reciprocal of the cell
thickness.

5.   ACKNOWLEDGMENTS

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APPENDIX B

FORMULATION AND PREDICTED PROPERTIES OF
NEMATIC EUTECTIC MIXTURES OF ESTERS*

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Techniques are described both for
formulating new nematic liquid crystal (LC)
eutectic mixtures and for calculating
several of their predicted properties.
Ester LC components from various structure
classes are used. Emphasis is placed on
obtaining mixtures which have relatively
short average molecular length, and which
are suitable for dynamic scattering electro-
optical applications. Examples are given of
binary eutectic mixtures made with LC esters
of essentially the same molecular length.
Selection rules are described for mixing
short length components, both from
homologous series and from different classes
of esters. Approximate class values of
birefringence, dielectric anisotropy, and
viscosity are assigned to each type of ester
structure, based on experimental results in
selected mixtures of short molecular length.
Properties of multi-component eutectic
mixtures are calculated, and comparisons are
shown between the predicted and the observed
values of melting point, clearpoint,
viscosity, dielectric anisotropy, and
birefringence of new ester mixtures
developed for dynamic scattering devices and
displays.

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Liquid Crystals and Ordered Fluids, American Chemical
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J. D. MARGERUM, A. M. LACKNER, et al

1. INTRODUCTION

Multicomponent liquid crystal (LC) mixtures are
generally needed to obtain a nematic phase with a
wide temperature range. In the formulation of
LCs for dynamic scattering applications, we have
shown that it is advantageous to use short
molecular length components to obtain low
viscosity and other favorable properties.[1-5]
However, special selection techniques are
required in choosing components in order to
prepare LC eutectic mixtures when combining short
length ester components of similar molecular
length. Otherwise, such components can act as
solid solutions and not give a lowered melting
point. It is also highly desirable to be able to
predict key anisotropic properties as well as the
nematic temperature range of each new
multicomponent mixture being considered for use.
In this paper both of these issues are addressed.
We describe selection rules for obtaining binary
eutectic mixtures with ester components of
essentially equal molecular length, and we show
how to use these LC pairs in the formulation of
multicomponent eutectic mixtures with relatively
short molecular length. We also show how we
assign approximate class values of birefringence
(Δn), dielectric anisotropy ($\Delta \varepsilon$), and viscosity
(η) to the various types of ester structures
being considered for use in our mixtures.
Finally, we compare actual experimental values
versus our predicted calculations of nematic

FORMULATION AND PROPERTIES OF EUTECTIC MIXTURES

melting point (mp) and clearpoint (clpt.), as
well as predicted values of Δn, $\Delta \epsilon$, and η at $25^{\circ}C$
for several multicomponent LC ester mixtures of
interest for dynamic scattering applications.

2. ___EXPERIMENTAL___

This study includes data on and calculations with
32 different classes of ester LC structures, with
specific reference to 95 individual components.
Both the classes and the individual compounds are
referred to here by a code nomenclature similar
to ones we have used previously.[1-5] Class codes
for various structures are shown in Figures 1, 2
and 3. The class structures which we reported
previously are shown in Figure 1. The class
structure and code of other ester compounds
synthesized by us more recently [6] are shown in
Figure 2. The structure and code for other
esters obtained commercially are given in Figure
3. The R and R' end groups in each class are
n-alkyl groups, and the specific compounds are
identified by numbers corresponding to the number
of carbon atoms in these alkyl groups. For
example, in the R-R' class p-n-heptylphenyl
p-n-butylbenzoate is represented by 7-4, while in
the RO-R' class p-ethoxyphenyl p-n-propylbenzoate
is 20-3. Thus in our code the dash, -, is for
the central phenyl benzoate structure, with
alternate central structures represented by S
for phenyl thiobenzoate, -[C] for phenyl
cyclohexanecarboxylate, [C]- for cyclohexyl

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STRUCTURE CLASS	CLASS CODE	REFERENCE
RO—〈〉—OOC—〈H〉—R'	RO-(C) R'	2, 3, 5
R—〈〉—OOC—〈〉—R'	R—R'	5
RO—〈〉—OOC—〈〉—R'	RO—R'	1, 3, 5
R—〈〉—OOC—〈〉—OR'	R—OR'	4, 5
RO—〈〉—OOC—〈〉—OR'	RO—OR'	3, 5
RO—〈〉—SOC—〈〉—R'	ROSR'	3, 5
R—〈〉—SOC—〈〉—OR'	RSOR'	5
RO—〈〉—SOC—〈〉—OR'	ROSOR'	3, 5
NC—〈〉—OOC—〈〉—R	NC—R	5
R—〈〉—OOC—〈〉—OOC—R'	R—OOCR'	5
RO—〈〉—OOC—〈〉—OOC—R'	RO—OOCR'	3, 5
R—〈〉—OOC—〈〉—OOC—〈〉—R'	R—OOCPR'	5
R—〈〉—OOC—〈Cl〉—OOC—〈〉—R'	R—(Cl)OOCPR'	3, 5
R—〈〉〈〉—OOC—〈〉—R'	RP—R'	5
R—〈〉—OOC—〈〉〈〉—R'	R—PR'	5
R—〈CN〉—OOC—〈〉〈〉—R'	R(CN)—PR'	3, 5
R—〈CN〉—OOC—〈〉〈〉—OR'	R(CN)—POR'	5

FIGURE 1 Structure and class code of esters
previously reported.
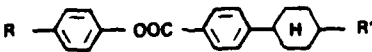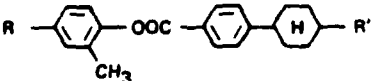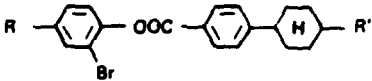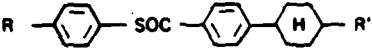
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FORMULATION AND PROPERTIES OF EUTECTIC MIXTURES

FIGURE 2   Structure and class code of other esters
synthesized[6]

benzoate, [C]-[C] for cyclohexyl
cyclohexanecarboxylate, and [Py]- for o-pyridyl
benzoate. Additional rings in the structure are
represented by P for phenyl and Y for cyclohexyl,
while only o-substituents are shown in
parenthesis, e.g. l(Br)-Y3 stands for o-bromo-p-
tolyl p-(4-propylcyclohexyl)benzoate.

The molecular length (L) of each compound is

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measured with a molecular model, and thermal
analysis data on mp, clpt. and heat of fusion
(ΔH_f) are obtained by differential scanning
calorimetry. In previous reports,[1-4] these
methods are described and the results were
tabulated for many of the compounds used in this
study. Table I shows the molecular length and
thermal properties of the additional esters used
here for eutectic mixture calculations.

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STRUCTURE CLASS	CLASS CODE	COMPOUNDS	SOURCE
R —◯— OOC —⬡— R'	R—[C] R'	5—[C] 5	ATOMERGIC
NC—◯— OOC —⬡— R	NC—[C] R	NC—[C] 5	ATOMERGIC
RO—◯— SOC —⬡— R'	ROS[C] R'	20S[C] 5	ATOMERGIC
R —◯— OOC —◯—⬡— R'	R—YR'	3—Y3	MERCK
R —◯— OOC —◯—⬡— R' (CN)	R(CN)—YR'	4(CN)—Y3	MERCK
R —⬡—◯— OOC —⬡— R'	RY—[C] R'	3Y—[C] 4	MERCK
R —⬡— OOC —◯—⬡— R'	R[C]—YR'	3[C]—Y2, 3[C]—Y4	MERCK
R —⬡— OOC —⬡—⬡— R'	R[C]—[C] YR'	3[C]—[C] Y4	MERCK

FIGURE 3   Structure and class code of commercial
esters[6]

FORMULATION AND PROPERTIES OF EUTECTIC MIXTURES

TABLE I   Thermal properties of components[a]

Component	L (Å)	mp ($^{\circ}$C)	Clpt. ($^{\circ}$C)	ΔH_f (kcal/mole)
10-4	19.70	61.8	24.6	5.99
10-01	17.52	123.8	20.0[b]	7.39
10-04	21.09	91.5	79.2	9.65
10-06	23.54	93.1	76.4	10.86
20-01	18.72	96.7	93.0	7.78
40-01	21.13	79.1	80.4	8.24
1S04	20.18	81.7	80.0	7.66
10S4	20.00	64.5	57.4	6.66
20S3	19.98	85.4	96.2	6.43
20S5	22.38	81.3	87.5	7.17
40S1	20.12	65.9	78.2	6.66
40S3	22.50	50.9	81.8	5.22
40S6	26.20	40.2	69.6	4.98
2-Y3	23.05	103.8	175.1	5.13
3-Y3	24.28	89.0	186.0	5.00
4-Y3	25.52	91.7	174.2	5.33
1SY3	22.53	120.4	219.0	4.45
3P-4	25.55	93.4	182.3	4.97
4-OOCP4	28.31	88.5	186.0	5.71
4-OOCY4	28.74	64.8	185.0	7.27

[a]These properties for the other components used in this study for eutectic calculations have been reported previously. (References 1-4).

[b]Estimated.

The experimental methods of measuring $\Delta\varepsilon$ and Δn are the same as reported previously,[1-4] except that no conductivity dopants are used. In the $\Delta\varepsilon$ measurements the field strength is 6.5 kG and the cells are 503μm thick. The value of the $\Delta\varepsilon$ measurement is often independent of the measuring frequency in the 100 to 10,000 Hz range, in which case the value reported is taken at 5,000 Hz. When the $\Delta\varepsilon$ values are observed to decrease with

increasing frequency, then a value at a lower frequency (e.g. 200,500 or 1000 Hz) is used in the range where $\Delta\epsilon$ is not changing with frequency. The flow viscosity measurements and assigned class viscosities are reported in other papers[1-7] from our laboratory.

The Schroeder-Van Laar relationship, equation 1, is used to estimate the crystal to nematic melting point and the mole fraction of the components in a eutectic mixture.

$$T_i = \frac{\Delta H_f}{\frac{\Delta H_f}{T_M} - R \ln x_i}, \qquad (1)$$

Where: T_i = upper end of the melting range of i in the mixture; ΔH_f = molar heat of fusion of pure compound i; T_M = melting point of pure compounds; x_i = mole fraction of component i in the mixture; and R = gas constant.

When Eq. 1 is satisfied for each component, the mixture will be a eutectic mixture -- assuming that ideal interaction occurs. This calculation, which is made with a computer program for multicomponent mixtures, is assumed to give approximately the correct composition for the actual eutectic mixture. If the mp is considerably higher than the calculated value, then a more accurate eutectic mixture can be determined experimentally by partial freezing

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fractionations of the calculated eutectic
mixture.[8]

The nematic to isotropic clearpoint (T_c) of
a multicomponent mixture can be estimated from
the composition and the clearpoints of the
individual components $(T_{c(i)})$:

$$T_c = \sum_{i=1}^{n} \left(X_i \; T_{c(i)} \right). \tag{2}$$

3. RESULTS AND DISCUSSION

3.1 Selection of Short Length Mixtures

Although ester mixtures with shorter average
molecular length (L) show superior dynamic
scattering properties over similar mixtures with
longer L, special care must be taken to select
short L components which will form eutectic
mixtures with one another. If the compounds are
too similar in structure and length they can form
a solid solution mixture rather than a eutectic
mixture. This is the case, for example, with a
mixture of 60-4 and 60-5 which show a melting
point between those of the two pure components
rather than one below both of them as is expected
from an eutectic mixture. Often this problem had
previously been avoided by selecting mixture
components which were each different in length by
at least two methylene groups. However,
multicomponent ester mixtures are needed to
obtain broad nematic temperature ranges, and when

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many components are used together it is very
difficult to obtain short mixture if each
component is two or more methylene groups

different in length from all of the others. To
circumvent this problem we have devised methods
of selecting equal length components which can be
used together in eutectic mixtures.[9]

One technique (Method I) is to use a binary
eutectic mixture consisting of equal length ester
components from a homologous series by selecting
components in which the alkyl end groups are
substantially different at the same molecular
position. Several sets of such binary mixtures
are listed in Table II under Method I. In
general if the number of carbon atoms in the
n-alkyl end groups are represented by R_a and R_a'
in compound A, and by R_b and R_b' in compound B,
then a binary eutectic mixture with A and B of
equal length (i.e. $R_a + R_a' = R_b + R_b'$) can be
made by selecting alkyl groups that differ by 2
carbons or more at each specific end of the
structure, i.e. $|R_a - R_b| \geq 2$ and $|R_a'-R_b'| \geq 2$.
This is illustrated for three different
homologous series in Table II, by combinations of
such as 20-3/40-1, 20S5/40S3, and 10-04/40-01.

Another technique (Method II) is to use a
binary eutectic mixture consisting of two
essentially equal length components from
different classes of esters. In the notation
above for compounds A and B of different classes,
binary eutectics can be made when

TABLE II   Binary LC eutectics with equal length components.

Components	Thermal Data[a]	Mole Fraction[b]	Nematic Temp. Range Calc.(°C)	Obs.(°C)
Method I				
20-3	1,3	0.515	53.0-60.6	52.1-61.9
40-1	1	0.484		
20-5	1,3	0.581	47.3-60.2	43.8-60.8
40-3	1	0.419		
2OS3	Table I	0.367	50.5-84.7	45.4-84.4
4OS1	Table I	0.633		
2OS5	Table I	0.256	39.4-83.3	39.2-75.5
4OS3	Table I	0.744		
1OS4	Table I	0.505	42.7-67.6	28.8-65.8
4OS1	Table I	0.495		
10-O4	Table I	0.366	66.0-80.0	64.8-81.2
40-O1	Table I	0.634		
Method II				
10-4	Table I	0.583	43.6-38.2[c]	43.1-39.0[c]
1OS4	Table I	0.417		
10-4	Table I	0.680	48.0-42.3[c]	49.5-38.2[c]
1SO4	Table I	0.320		
1OS5	3	0.358	24.8-70.9	27.9-68.4
10-[c]5	2,3	0.642		
20-3	1,3	0.319	36.4-74.6	37.8-73.9
20-[c]3	2,3	0.681		
40-6	1,3	0.412	20.7-61.1	21.9-61.8
4OS6	Table I	0.588		

[a]Source of experimental mp, clpt., ΔH_f, and molecular length.
[b]Calculated mole fraction from Schroeder-Van Laar equation.
[c]Monotropic mixture.

$R_a + R_a' = R_b + R_b'$. In the cases shown in Table II, Method II, the alkyl groups can be the same at each specific end of the structure,

e.g. $R_a = R_b$ and $R_a' = R_b'$ in binary combinations such as 10-4/10S4 and 20-3/20-[C]3, etc. However, it is also all right if $R_a \neq R_b$ when other equal length components from these classes are combined, e.g. 20-3/10-[C]4. In some cases (not shown in Table II) it is necessary to use a combination of Methods I and II. For example the calculated binary mixture for 60-01/60S01 gives a solid state solution, while the mixture 60-01/10S06 gives an eutectic type depressed melting point.

Each of the binary sets in Table II is formulated with the mole fractions calculated by the Schroeder-Van Laar relationship (equation 1), and experimentally each set is a eutectic type mixture with a melting point similar to the calculated (ideal) value. The observed clearpoints are also shown for these binaries in Table II, and are all close to the ideal values calculated by equation 2. However, the clearpoints are often near (usually slightly below) the values calculated whether or not the mixture shows eutectic properties.

The binary set of LC components described by our methods I and II, and illustrated by the examples in Table II, can be used in the formulation of multicomponent LC eutectic mixtures with relatively short C by combining one or more sets of these short length binaries together with other short length ester LC components. Combining sets of binary mixtures

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with common components can give tertiary and
quaternary eutectics of equal length LCs. Our
selection rules for the other components are that
in general they should differ from the binaries
and from one another either by being from a
different ester class or by being about two
methylene groups (2.5A) or more different in
length. An exception is that some very short
length components of the same class can be used
together when differing by only one methylene
group if this difference is between a methyl and
an ethyl end group. As explained in the
experimental section, the mole fraction
composition is calculated for each new
multicomponent eutectic by using the Schroeder-
Van Laar equation. This is assumed to give a
relatively close approximation to the true
eutectic composition (if it exists for the
components selected), and this theoretical
composition is the one that we use to test the
mixture.

A very short £ eutectic mixture of RO-R'
components is the HRL-2N42 mixture whose
composition and properties are shown in Table
III. This five component homologous mixture
contains two set of Method I binaries (20-3/40-1
and 20-5/40-3) along with 10-1, which is a
pseudo-nematic component.[1] The observed nematic
range is actually better than the calculated
range, and this particular mixture is used
extensively in the present work as a host LC for

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TABLE III   RO-R' eutectic mixture HRL-2N42.

Composition[1]		Characteristics		
Components	Mole. Fraction	Property	Calc.	Obs.
10-1	0.112	mp(^{o}C)	28.8	5.3
20-3	0.222	Clpt.(^{o}C)	57.0	57.7
20-5	0.283	Length($\overset{o}{A}$)	20.39	-
40-1	0.191	$\Delta n(23^{o})$	-	0.158
40-3	0.192	$\Delta\varepsilon(25^{o})$	-	-0.21
		$n(25^{o},cP)$	-	32.6

experiments in determining the relative class Δn
and $\Delta\varepsilon$ contributions of other LC components.
Several other such RO-R' eutectic mixtures have
been described[1] which include equal length binary
set components. Another relatively short L
eutectic mixture from a different homologous
group is the 7-component RO-OR' mixture HRL-2N54
shown in Table IV. It contains the two binary
sets 10-04/40-01 and 10-06/60-01. It also
contains the short length components 10-01 and
20-01. The observed nematic range of 2N54 is
wider than the calculated one. Table V shows an
example of the short length thioester eutectic
mixture HRL-5N3. This is a 7-component eutectic
made with two classes of thioester LCs. It
includes three components of the same length
(corresponding to three binary sets), namely
10S4/20S3/40S1. The 5N3 mixture has a
nematic range very close to the calculated range.
Before examining other multi-component eutectics
formulated with our selection rules, the
following sections describe the assignments of

TABLE IV   RO-OR' eutectic mixture HRL-2N54.

Composition			Characteristics		
Components	Ref.	Mole. Fraction	Property	Calc.	Obs.
10-01	I	0.145	mp(^{o}C)	24.9	-
10-04	I	0.051	Clpt.(^{o}C)	78.3	80.2
10-06	I	0.033	Length(Å)	23.23	-
20-01	I	0.078	Δn(23°C)	-	0.171
40-01	I	0.118	$\Delta\varepsilon$(25°)	-	-0.35
40-05	3	0.291	η(25°,cP)	-	106
60-C1	3	0.385			

TABLE V   Thioester eutectic mixture HRL-5N3.

Composition			Characteristics		
Components	Ref.	Mole Fraction	Property	Calc.	Obs.
10S4	I	0.094	mp(^{o}C)	-0.6	-
10S5	3	0.123	Clpt.(^{o}C)	78.6	76.0
10SO6	3	0.110	Length(Å)	23.05	-
20S3	I	0.058			
40S1	I	0.097			
40S3	I	0.217			
40S6	I	0.302			

class values of Δn, $\Delta\varepsilon$, and η. These are used in our calculations to predict these anisotropic properties, as well as the nematic temperature range, for new mixtures.

3.2 Assignment of Class Birefringence

The Δn of a nematic ester LC depends mainly on the class of the ester structure, and somewhat upon the length of it alkyl end groups. This has been shown previously for 100% mixtures of RO-R', RO-[C]R', and R-OR' structures.[1,2,4] Because it

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is not easy to prepare 100% mixtures for each
ester class structure of interest, we instead
obtain approximate Δn class values by measuring
the Δn of mixtures containing specific components
of a given class added to a standard host LC.
The RO-R' mixture 2N42 is used as the host, and
it is generally mixed with 25 mole percent of the
components being studied. The Δn contribution of
the added component is estimated by the
approximation of simply subtracting out the
contribution due to the host. Thus with 25%
added components to 75% 2N42 at 23°C, the Δn_{calc}
for the added components is obtained from
equation 3.

$$\Delta n_{obs} = 0.25(\Delta n_{calc}) + 0.75(0.158) \qquad (3)$$

For example a Δn_{obs} of 0.170 is measured when 25%
of 40S3 is added to 2N42, giving a Δn_{calc} of
0.206 from which we assign ROSR' a Δn_{class} of
0.21 in the environment of a short length RO-R'
host LC. This is the manner in which most of the
Δn_{class} values are assigned for the 30 different
ester classes shown in Table VI. In several
cases these extrapolated Δn_{class} values are found
to be in good agreement with Δn_{obs} for 100%
mixtures of the same class, as noted in Table VI
for RO-OR', R-(Cl)OOCPR', and RO-[C]R' mixtures.
The Δn_{class} assignments for RO-R' and R-OR'
mixtures are estimated from 100% mixtures at an
L of 22 A. The Δn_{class} for R-R' is taken from
the average value obtained from measuring three

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TABLE VI Assignment of class birefringence values.

Class	Δn_{class}[a]	Components Measured[b]
RP-R', R-PR'	0.25	3P-4, 5P-4, 5-P5
R(CN)-PR'	0.25	7(CN)-P5
R(CN)-POR'	0.23	4(CN)-PO3
ROSOR'	0.23	10SO4, 10SO6
RSYR'	0.23	1SY3 (10%)
ROSR'	0.21	4OS3
RSOR'	0.21	1SO6
R-OOCPR'	0.18	2-OOCP2, 4-OOCP4
RO-OR'	0.17	4O-O5, 6O-O5;(100% 2N54)
RO-YR'	0.17	2O-Y3, 2O-Y5
ROOCPPOR'	0.17	3OOCPPO6
R-(Cl)OOCPR'	0.16	2-(Cl)OOCP2,5-(Cl)OOCP5 (also, 100% 2P37)
R-YR'	0.15	2-Y3,4-Y3
RO-R'	0.15	2N42;2N43 etc.[1] (100%)
R-OR'	0.14	2P13;etc.[4] (100%)
R(Br)-YR'	0.14	1(Br)-Y3
NC-R	0.13	NC-4,NC-7
R(CH$_3$)-YR'	0.13	1(CH$_3$)-Y3
RO-OOCR'	0.13	4O-OOC4,6O-OOC5
R-OOCR'	0.12	3-OOC5,7-OOC5
R(CN)-YR'	0.11	4(CN)-Y3
ROS[C]R'	0.11	2OS[C]5
R-OOCYR'	0.11	4-OOCY4
RO-[C]R'	0.09	2O-[C]5 (also,100%6N7)[2]
NC-[C]R	0.08	NC-[C]5
R[C]-YR'	0.08	3[C]-Y2, 3[C]-Y4
RY-[C]R'	0.07	3Y-[C]4, 3Y-[C]5
R-R'	0.07	7-6; 7-4; 5-5
R-[C]R'	0.04	5-[C]5
R[C]-[C]YR'	0.04	3[C]-[C]Y4

[a]Extrapolated value of Δn at 23°C for ester classes in environment of short length RO-R mixtures.

[b]Measured in HRL-2N42 with 25% concentration of components (total) unless noted otherwise.

different mixtures of R-R' components in the host. In many cases more than one component of a

given class is needed to obtain a 25% solution,
such as the use of 10S04 and 10S06 together
in 2N42. When such component mixtures are used
for the additives, the mole percent of each
individual component is the same as those
reported in our viscosity studies.[5,6]

Higher birefringence values in LC structures
are generally related to higher molecular
polarizability along the director axis. This is
particularly noticeable in Table VI for the
Δn_{class} values of biphenyl ester and thioester
structures. Lower Δn_{class} values are found when
cyclohexyl rings replace phenyl rings and when
alkyl groups replace alkoxy groups. Thus the
ester class R[C]-[C]YR' with neither phenyl nor
alkoxy groups has the lowest Δn_{class} in Table VI.

3.3 Assignment of Class Dielectric Anisotropy

As in the birefringence studies, we assign class
values of $\Delta \varepsilon$ based largely on measurements of
selected components mixed with the RO-R' host
2N42. We are aware that intermolecular
association effects in LCs can substantially
alter observed values of $\Delta \varepsilon$, as was noted
previously particularly for longer length R-OR'
mixtures.[4] Thus, in the strict sense our
extrapolated $\Delta \varepsilon_{class}$ values from measurements
in 2N42 represent just the contributions of the
added components in the environment of the short
length RO-R' host. When the final mixture

consists of 25% added components and 75% 2N42,
then the $\Delta\epsilon_{calc}$ for the additives at 25°C is
obtained from equation 4:

$$\Delta\epsilon_{obs} = 0.25\ (\Delta\epsilon_{calc}) - 0.75\ (0.21) \qquad (4)$$

For example, a $\Delta\epsilon_{obs}$ of 0.138 is measured when
25 mole percent of $1(CH_3)$-Y3 is added to 2N42,
giving a $\Delta\epsilon_{calc}$ of 1.18 from which we assign
$R(CH_3)$-YR' a $\Delta\epsilon_{class}$ of 1.2. A list is shown
in Table VII for the assigned $\Delta\epsilon_{class}$ values of
23 different class ester structures. As
indicated in Table VII, most of the assignments
are made from measurements of 10 to 25% additives
in 2N42. The $\Delta\epsilon_{class}$ values for the RO-R', and
R-OR' structures are taken from the 100% mixtures
of these previously studied. [1,4]

Several generalizations can be noted from
the relative $\Delta\epsilon_{class}$ values in Table VII. The
thiobenzoate structures are all considerably more
positive in $\Delta\epsilon_{class}$ values then the
corresponding benzoate structures, e.g.
RSYR'(1.6) vs. R-YR'(0.6), ROSOR'(0.4) vs.
RO-OR'(-0.3), and ROSR'(0.0) vs. RO-R'(-0.2).
Use of a cyclohexanecarboxylate group in place of
a benzoate group gives a considerably more
negative value of $\Delta\epsilon_{class}$, e.g. R-OOCYR'(0.3)
vs. R-OOCPR'(7.3), RO-[C]R'(-2.1) vs.
RO-R'(-0.2), and R-[C]R'(-1.2) vs. R-R'(0.1).
These results, which are summarized schematically
in Figure 4 for Δn and η as well as $\Delta\epsilon$, are

TABLE VII   Assignment of class dielectric anisotropy values.

Class	$\Delta\varepsilon_{class}$[a]	Components Measured	Concn.[b]
NC-[C]R	19.8	NC-[C]5	25%
R-(Cl)OOCPR'	7.9(4.7)[c]	2-(Cl)OOCP2,5-(Cl)OOCP5	10%
R-OOCPR'	7.3(4.7)[c]	2-OOCP2, 4-OOCP4	25%
RSYR'	1.6	1SY3	12.5%
R(CH3)-YR'	1.2	1(CH3)-Y3	25%
RP-R', R-PR'	0.8	3P-4, 5P-4, 5-P5	25%
R-YR'	0.6	2-Y3, 4-Y3, 2-Y5	25%
ROSOR'	0.4	1OS4, 1OSO6	25%
R-OOCYR'	0.3	4-OOCY4	12.5%
R-OR'	0.2	2P13, etc.[4]	100%
RO-YR'	0.1	2O-Y3, 2O-Y5	25%
R-R'	0.1	7-4	25%
ROSR'	0.0	4OS3	25%
ROOCPPOR'	0.0	3OOCPPO6	25%
RO-R'	-0.2	2N42; 2N43; etc.[1]	100%
RO-OR'	-0.3	6O-Ol; 4O-O5, 6O-O5	25%
R(Br)-YR'	-0.8	1(Br)-Y3	25%
RO-OOCR'	-1.0	4O-OOC4, 6O-OOC5	25%
R-[C]R'	-1.2(-0.3)[c]	5-[C]5	25%
RO-[C]R'	-2.1(-1.4)[c]	2O-[C]3	25%
(Py)-POR	-2.5	(Py)-PO5	10%
R(CN)-PR'	-5.4(-3.7)[c]	7(CN)-P5	25%
R(CN)-YR'	-6.5(-3.7)[c]	4(CN)-Y3	10%

[a] Extrapolated value of $\Delta\varepsilon$ at 25°C for ester classes in environment of short length RO-R mixtures.

[b] Concentration of components (total) added to HRL-2N42 for $\Delta\varepsilon$ measurement.

[c] $\Delta\varepsilon'_{class}$ values extrapolated from 25°C measurements of $\Delta\varepsilon$ for the components in the RO-[C]R' mixture HRL-6N7.

consistent with the relative polarizability along the long axis of these molecules.

In Table VII we also note several $\Delta\varepsilon'_{class}$ values calculated for components measured in the short length RO-[C]R' mixture HRL-6N7. These $\Delta\varepsilon'_{class}$ values are all smaller in magnitude
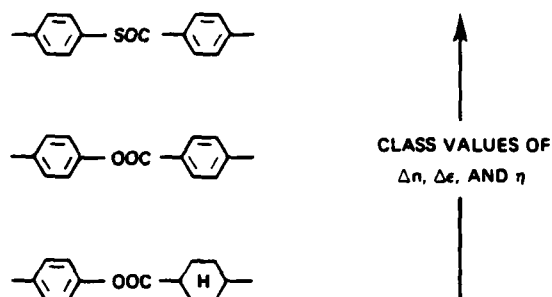
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FIGURE 4   Central structure effect on
relative class values, showing
direction of positive increase

(positive or negative) than the $\Delta\varepsilon_{class}$ values
measured in 2N42. We do not yet know what causes
the differences between our calculated $\Delta\varepsilon_{class}$
and $\Delta\varepsilon'_{class}$ values. Each molecule in the 2N42
host has two phenyl rings which should provide a
strongly positive magnetic anisotropy and
correspondingly good magnetic field alignment
along the LC direction in the $\Delta\varepsilon$ measurements.
Each molecule in the 6N7 host has one phenyl ring
and one cyclohexyl ring, resulting in a
substantially reduced magnetic anisotropy as
compared to molecules with two phenyl rings.[10]
However, because our measured $\Delta\varepsilon$ values are not
strongly affected by variations in the magnetic
field strength between 3.8 to 6.9 kG, we believe
that the 6N7 is nearly fully aligned at the
6.5 kG setting used in our experiments. Perhaps
the molecular axis of a guest additive is aligned
at a different angle with respect to the director

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of the 6N7 host than that of the 2N42 host. Or,
maybe the magnetic field alignment direction is
off-axis from the LC director in 6N7. These are
only speculations, and additional studies will be
necessary to determine the source of the
$\Delta\varepsilon_{class}$ and $\Delta\varepsilon'_{class}$ differences.

3.4 Assignment of Class Viscosity

The assignment of relative values of class
viscosity for 18 different ester classes (in an
RO-R' host LC) has been reported previously.[5]
The class viscosities of many additional classes
of esters are assigned similarly in a new paper.[6]
In nearly every case these η_{class} values are
assigned by extrapolating the effect of 10 to 25%
of the component on the flow viscosity of 2N42 at
25°C. Thus, these η_{class} values are just
relative values comparing the effect of each
structural class on the η of a standard short
length RO-R' mixture. In an environment
different from this type of RO-R' mixture, the
additives would be expected to show a different
η_{class}. Nevertheless, because most of the
multi-component mixtures which we are studying
contain several short length RO-R' components,
the η_{class} values derived from 2N42 are in fact
quite useful in predicting the viscosity of new
eutectic mixtures, as noted below.

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3.5 Formulation and Predicted Properties of Mixtures

Our Method I of using equal length binary sets of short length LC components in multicomponent homologous mixtures is illustrated by previously reported RO-R' mixtures[1] HRL-2N42, -2N43, -2N44, and -2N48, a well as the R-OR mixture[4] HRL-2P21. In the RO-R' mixtures the binary sets 20-3/40-1 and 20-5/40-3 are used in 2N42 and 2N43, while 20-5/40-3 is used in 2N44, and 60-5/80-3 is used in 2N48. In the R-OR' mixture the binary set 3-05/7-01 is used.

Our Method II of using equal length binary sets of different class LCs in multicomponent mixtures is illustrated by several mixtures previously described.[3] In particular: HRL-2N52 contains the binary sets 20-3/10-00C3 and 40-05/40-00C4, HRL-25N4 contains 60-01/10S06, HRL-26N3 contains the tertiary set 60-5/60-[C]5/80-3, HRL-26N4 contains the tertiary set 20-3/20-[C]3/10-00C3, and HRL-256N5 contains this same 20-3/20-[C]3/10-00C3 set along with 60-01/10S06. In Table VII we show the overall class component compositions for these mixtures (along with HRL-246N1) and we compare our calculated values of mp, clpt., Δn, $\Delta \epsilon$, and η with our observed values. The melting point and clearpoint are calculated using equations 1 and 2, respectively, while the other properties are estimated simply by summing the total mole fraction of each class (x_j) times its assigned

class value (equations 5-7).

$$\Delta n_{mix} = \sum (\Delta n_{class})_j \cdot x_j \qquad (5)$$

$$\Delta \varepsilon_{mix} = \sum (\Delta \varepsilon_{class})_j \cdot x_j \qquad (6)$$

$$\eta_{mix} = \sum (\eta_{class})_j \cdot x_j \qquad (7)$$

The assigned class values of Δn and $\Delta \varepsilon$ are taken from Tables VI and VII, respectively, while the η_{class} values are taken from other publications.[5,6] For each eutectic mixture composition calculated by the Schroeder-Van Laar equation (e.g. all in Table VIII except HRL-256N5) our computer is programmed to calculate the other properties as well. The computer contains a file on the mp, clpt, ΔH_f, L, and class values of Δn, $\Delta \varepsilon$, and η for each component. The program calculates the mole fraction of each component for the idealized eutectic mixture, and these mole fractions are used to calculate the predicted values of Δn, $\Delta \varepsilon$, and η for this mixture.

Most of the properties calculated for the mixture in Table VIII are fairly close to their observed values, indicating the general utility of using this technique to predict properties of new mixtures. The observed mps for 2N52, 25N4, and 26N3 are within 5° of those calculated, but both 26N4 and 246N1 have considerably higher observed than calculated mps due to small amounts of crystals that remelt near room temperature after the samples are stored for long periods at $-40^{\circ}C$. This indicates that the calculated

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TABLE VIII   Calculated and observed properties of prior mixtures.[3]

Component Classes	Mole Fractions in HRL Mixtures					
	2N52	25N4	26N3	26N4	246N1	256N5
RO-R'	0.384	0.420	0.266	0.228	0.181	0.149
RO-OR'	0.315	0.270	0.065	0.194	0.157	0.263
RO-[c]R'			0.500	0.222	0.390	0.142
ROSR'		0.155				0.142
ROSOR'		0.155				0.094
RO-OOCR'	0.302			0.354		0.210
R-(Cl)OOCPR'			0.169			
R(CN)-PR'					0.272	

Properties		2N52	25N4	26N3	26N4	246N1	256N5
Length ($\AA$)		24.9	23.9	26.4	23.3	26.3	23.3
mp	Calc.	3.0	-0.9	-15.0	6.7	1.3	-
	Obs.	7.0	5.0	-20.0	21.0	19.0	-9.0
Clpt.	Calc.	73.0	74.7	77.5	78.0	83.4	-
	Obs.	71.9	71.6	75.8	77.0	81.0	77.4
Δn	Calc.	0.15	0.18	0.12	0.13	0.16	0.16
	Obs.	0.150	0.169	0.118	0.141	0.143	0.158
$\Delta \varepsilon$	Calc.	-0.5	-0.1	0.2	-0.9	-2.4	-0.6
	Obs.	-0.45	-0.13	0.06	-0.96	-1.55	-0.49
η	Calc.	63	58	49	54	80	59
	Obs.	64.2	59.2	47.8	49.3	66.6	58.2

eutectic composition of 26N4 and 246N1 is probably slightly different than the true eutectic obtainable with these components.   The observed clearpoints in Table VIII are all only about 1 to 3° lower than those calculated.   Such differences are generally the case, and are probably indicative of some non-ideality of the mixtures.   The observed and calculated Δn are in good agreement, generally within 0.01 of one another.   The observed $\Delta \varepsilon$ are in good agreement with the calculated values for 2N52, 25N4, 26N4,

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and 256N5, but differ slightly for the 26N3 and
considerably for the 246N1 mixture. The strongly
positive $\Delta\epsilon$ component 5-(Cl)OOCP5 is present in
26N3, and as indicated in Table VII its $\Delta\epsilon_{class}$
of 7.3 (in a RO-R' mixture) is much higher than
its $\Delta\epsilon'_{class}$ of 3.2 measured in a RO-[C]R'
mixture--which class makes up 50% of 26N3. The
strongly negative $\Delta\epsilon$ component 7(CN)-P5 is
present in 246N1, and its $\Delta\epsilon_{class}$ of -5.4 is
lower than its $\Delta\epsilon'_{class}$ of -3.8. As discussed
above, the presence of the RO-[C]R' molecules in
the mixtures alters the $\Delta\epsilon$ measurements. The
observed values of η are in good agreement with
the calculated values for 2N52, 25N4, 26N3, and
256N5, and are lower than those calculated for
26N4 and 246N1. Thus, despite the limitations
inherent in using η_{class} values, we find that
generally the η_{mix} calculated for many ester
mixtures is equal to or slightly higher than the
observed values.

Six new eutectic ester mixture compositions
are shown in Table IX to illustrate further our
techniques of formulating short length ester
mixtures with improved properties for dynamic
scattering applications.[7] Their predicted (i.e.
calculated) versus their observed properties are
shown in Table X. In these formulations we are
seeking a wide nematic range (0 to 75°C, or
better), a relatively low viscosity
$(\eta_{250} < 40$ cP), and a slightly negative $\Delta\epsilon$.
Extensive use is made of our formulation methods

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I and II (both separately and combined) in order
to obtain short length mixtures, as indicated by
the following list of equal length binary,
tertiary, and quaternary combinations used:

HRL Mixtures	Equal Length Combinations
2456N1 ⎤ 256N13 ⎥ 256N19 ⎦	⎡20-3/40-1/20-[C]3, ⎢20-5/40-3/20-[C]5, ⎣10-[C]5/10S5
26N25	20-3/20-[C]3/10-00C3, 20-5/20-[C]5
26N35	20-3/40-1/20-[C]3/10-00C3, 20-5/40-3/20-[C]5
26N36	20-3/40-1, 20-5/40-3/20-[C]5

The observed mps and clpts. in Table X are all
fairly close to our predicted values for these
eutectic mixtures. The observed Δn values are in
excellent agreement with the calculated values.
The observed $\Delta\varepsilon$ are generally slightly less
negative than the calculated values, apparently
due to the presence of substantial percentages of
RO-[C]R' components, as discussed above. The
observed η values are all close to the calculated
values, ranging from 7 to 14% lower than
predicted. After adding appropriate dopants with

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TABLE IX   Compositions of new eutectic mixture.

Component	Ref.	Mole Fraction of Component in HRL Mixture					
		2456N1	256N13	256N19	26N25	26N35	26N36
20-3	1	0.054	0.051	0.050	0.061	0.054	0.057
20-5	1	0.058	0.055	0.053	0.067	0.058	0.062
40-1	1	0.037	0.034	0.033	-	0.037	0.039
40-3	1	0.034	0.032	0.031	-	0.034	0.036
40-6	1	-	-	-	-	-	0.110
60-3	1	0.163	0.156	0.152	-	-	-
60-5	1	-		-	0.229	0.204	0.214
10-[C]5	2	0.246	0.236	0.232	0.272	0.245	0.256
20-[C]3	2	0.125	0.118	0.115	0.142	0.124	-
20-[C]5	2	0.066	0.062	0.060	0.077	0.066	0.070
10S5	3	0.133	0.128	0.125	-	-	-
10-OOC3	3	-	-	-	0.037	0.032	-
40-OOC4	3	-	-	-	0.045	-	-
2-Y3	6	-	0.059	-	-	-	-
3-Y3	6	-	-	0.082	-	0.087	0.091
4-Y3	6	-	0.065	-	-	-	-
1SY3	6	-	-	0.066	-	-	-
3P-4	5	0.082	-	-	-	-	-
4-OOCP4	5	-	-	-	0.070	-	0.065
4-OOCY4	6	-	-	-	-	0.059	-

high conductivity anisotropy, all of these new mixtures have favorable dynamic scattering properties. The 26N25, 26N35, and 26N36 mixtures with redox dopants [3,11] are particularly useful as improved LCs for long life dc-activated dynamic scattering at elevated temperatures.[7]

4.   CONCLUSIONS

1.   Multicomponent ester eutectic mixtures with short average molecular length can be prepared by including selected binary, tertiary

FORMULATION AND PROPERTIES OF EUTECTIC MIXTURES

TABLE X   Calculated and observed properties of
new eutectic mixtures.

Properties		HRL Mixtures					
		2456N1	256N13	256N19	26N25	26N35	26N36
Length (Å)		22.1	22.1	22.0	23.2	23.0	23.8
mp	Calc.	-5.1	-6.2	-6.8	-2.3	-5.2	-4.0
	Obs.	0	-5	-15	0	-4	-13
Clpt.	Calc.	78.3	82.4	88.5	79.2	86.3	83.4
	Obs.	73.8	77.7	84.5	73.9	81.9	77.6
Δn	Calc.	0.14	0.13	0.13	0.12	0.12	0.13
	Obs.	0.133	0.127	0.133	0.120	0.12	0.13
$\Delta\epsilon$	Calc.	-0.9	-0.9	-0.8	-0.7	-1.0	-0.3
	Obs.	-0.70	-0.60	-0.52	-0.57	-0.70	-0.28
η	Calc.	30	31	32	36	34	38
	Obs.	27	28.4	28.7	31	32	35.6

and quaternary sets of short length ester LC
components of essentially equal molecular length.
Two methods are found to be suitable for
selecting eutectic LC binary sets (and
combinations thereof to give tertiary and
quaternary sets) with equal length components.
Guidelines are described for combining these
binary sets together with other components, and
such multicomponent ester eutectics are each
found to have a nematic temperature range close
to the theoretical one calculated by applying the
Schroeder-Van Laar equation.

2.   Approximate class values of
birefringence and dielectric anisotropy (as well
as viscosity, reported elsewhere) can be assigned
by measuring the effect of specific class
components on these properties in a standard

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short length RO-R' mixture. These class values
are found to be useful in several ways. Their
relative magnitude provides a basis for
qualitative comparisons of structural effects on
these anisotropies. The assigned class values
are also very useful in predicting, with fairly
good accuracy, the room temperature values of Δn,
$\Delta \varepsilon$, and η for new multicomponent ester mixtures.

    3. Several new short length,
multicomponent, eutectic mixtures of ester LCs
are successfully formulated with the properties
desired for dynamic scattering applications.
These new mixtures have a wide nematic range,
relatively low viscosity, slightly negative
dielectric anisotropy, and good compatibility
with redox dopants for dc-activation.

5. ACKNOWLEDGMENTS

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APPENDIX C

EFFECTS OF CYCLOHEXYL GROUPS AND ORTHO-SUBSTITUENTS ON THE VISCOSITY OF ESTER LIQUID CRYSTAL COMPONENTS*

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Structural effects on the relative viscosity
of liquid crystal ester components are
studied by capillary flow viscosity
measurements of each component as an additive
(10 to 25%) in a standard nematic mixture of
short length 4-alkoxyphenyl 4-alkylbenzoates.
An approximate class viscosity at 25°C is
calculated and assigned to each additive
component, indicative of its viscosity
contribution in the environment of the phenyl
benzoate mixture. Studies are made on the
viscosity effects of replacing benzene rings
with cyclohexane rings, and of using various
ortho-substituents on phenyl groups. All of
the additive components are esters or
thioesters, including several newly
synthesized compounds. The effect of a
cyclohexyl group is strongly dependent on its
position in the structure. The class
viscosity values show a large decrease when
cyclohexanecarboxlate replaces benzoate, only
a modest decrease when cyclohexylbenzoate
replaces biphenylcarboxylate, and a slight
increase when a cyclohexyl ester replaces a
phenyl ester. Although o-groups can be used
effectively to alter the dielectric

anisotropy and modify the nematic range of a
component, they increase the class viscosity
values substantially, with the magnitude of
the viscosity effect in the following
approximate order from several o-groups:
Br > CN > CH_3 > pyridyl > Cl.

1. INTRODUCTION

The effects of chemical structure on liquid
crystal (LC) viscosity (η) are important
considerations in the selection of components for
nematic mixtures used in display applications.
For example, it is desirable to be able to predict
the viscosity of a new multicomponent LC mixture
accurately enough to decide whether or not it is
worthwhile to make up a calculated eutectic
mixture for study. We have previously described
the assignment of approximate class viscosity
values (n_{class}) to eighteen different classes of
ester LC structures[1], and we have shown that these
n_{class} values are useful in predicting the
viscosity of new mixtures.[1,2] We are particularly
interested in developing additional new LC
mixtures with low viscosity, negative dielectric
anisotropy, and wide nematic temperature range for
both dynamic scattering and field-effect display
applications. In working toward these goals, we
report here more detailed studies on the viscosity
effect of structural changes in LC esters in which
phenyl groups are replaced by cyclohexyl groups,
or in which o-substituents are used on phenyl

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groups. Twenty additional ester structures are assigned η_{class} values, and systematic comparisons are made on the changes in class viscosities with structural variations.

2. EXPERIMENTAL

Flow viscosity studies are made with 29 different ester LC components. These are studied as additives in a standard mixture (HRL-2N42) of five 4-alkoxyphenyl 4-alkylbenzoate esters.[1,2,3] The capillary flow viscosity and density data are taken at 25°C with 10 to 25 mole percent of the components added to HRL-2N42, as previously described.[1] The code symbols used here for the individual compounds and their general classes are similar to those defined previously.[1-5] In our code a dash, -, is for the central phenyl benzoate structure, with alternate central structures represented by S for phenyl thiobenzoate, -[C] for phenyl cyclohexanecarboxylate, [C]- for cyclohexyl benzoate, [C]-[C] for cyclohexyl cyclohexanecarboxylate, and [Py]- for o-pyridyl benzoate. Additional rings in the structure are represented by P for phenyl and Y for cyclohexyl, while only o-substituents are shown in parenthesis, e.g. 1(Br)-Y3 stands for o-bromo-p-tolyl p-(4-propylcyclohexyl)benzoate. Twenty of the 29 LC compounds investigated are synthesized, and the other nine are commercial samples obtained from either E. Merck or from Atomergic Chemetals.

Nineteen of the synthesized esters are prepared by reacting purified samples of commercially available (Aldrich) phenols or thiophenols with acid chlorides, whose acid intermediates are obtained by hydrolysis of the corresponding nitrile LC compounds (E. Merck). The other di-ester (4-OOCY4) is made using intermediates prepared as described before, namely the mono-ester 4-OH phenol[1] and the trans-4-butylcyclohexanecarbonyl chloride.[4] Thermal analysis data on the melting point (mp), clearpoint (clpt), and molar heat of fusion (ΔH_f) of the new compounds are obtained by differential scanning calorimetry.[3] The purity of all of the LCs is checked by thin layer chromatography and by liquid chromatography.[1-3]

3. RESULT AND DISCUSSION

3.1 LC Compounds Synthesized

The abbreviation code, structure, melting point, clearpoint, and molar heat of fusion of the 20 LC compounds synthesized are given in Table I. The first 10 of these are all variations of similar three ring structures with the same alkyl end groups (e.g. 1-P3, 1SP3, 1-Y3, etc) and essentially the same molecular length. These structural variations are chosen not only to observe the viscosity effects of thioesters,

VISCOSITY OF ESTER LIQUID CRYSTAL COMPONENTS

Table I.   New LC Components Synthesized

CODE	STRUCTURE	mp (°C)	Clpt. (°C)	ΔH_f (kcal/mole)
1-P3	CH_3—⬡—OOC—⬡—⬡—C_3H_7	126	199	7.26
1 S P3	CH_3—⬡—SOC—⬡—⬡—C_3H_7	126	235	6.12
1-Y3	CH_3—⬡—OOC—⬡—(H)—C_3H_7	121	188	5.84
1 S Y3	CH_3—⬡—SOC—⬡—(H)—C_3H_7	120	224	4.72
1(CH$_3$)-Y3	CH_3—⬡(CH_3)—OOC—⬡—(H)—C_3H_7	79	118	5.18
1(Br)-Y3	CH_3—⬡(Br)—OOC—⬡—(H)—C_3H_7	97	119	7.12
1(C)-P3	CH_3—(H)—OOC—⬡—⬡—C_3H_7	94	126	4.89
1(C)-Y3	CH_3—(H)—OOC—⬡—(H)—C_3H_7	91	129	6.35
1-(C)Y3	CH_3—⬡—OOC—(H)—(H)—C_3H_7	53(96)[a]	204	5.93
1(C)-(C)Y3	CH_3—(H)—OOC—(H)—(H)—C_3H_7	67(129)[a]	153	7.72
2-Y3	C_2H_5—⬡—OOC—⬡—(H)—C_3H_7	104	175	5.13
2-Y5	C_2H_5—⬡—OOC—⬡—(H)—C_5H_{11}	92	172	6.32
4-Y3	C_4H_9—⬡—OOC—⬡—(H)—C_3H_7	92	174	5.33
4-OOCY4	C_4H_9—⬡—OOC—⬡—OOC—(H)—C_4H_9	62(65)[a]	185	7.27
20-P3	C_2H_5O—⬡—OOC—⬡—⬡—C_3H_7	128	235	7.88
20-P5	C_2H_5O—⬡—OOC—⬡—⬡—C_5H_{11}	126	220	6.08
20-Y3	C_2H_5O—⬡—OOC—⬡—(H)—C_3H_7	127	223	6.39
20-Y5	C_2H_5O—⬡—OOC—⬡—(H)—C_5H_{11}	106	215	6.39
[P$_y$]-P05	(N⬡)—OOC—⬡—⬡—OC_5H_{11}	78(86)[a]	114	3.65
[P$_y$]-(C)Y3	(N⬡)—OOC—(H)—(H)—C_3H_7	108	118	8.51

[a] SMECTIC TO NEMATIC TRANSITION

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cyclohexane groups, and o-substituents, but also
to note these structural effects on the nematic
temperature range, the birefringence (Δn), and the
dielectric anisotropy ($\Delta \epsilon$). Studies on Δn and $\Delta \epsilon$
are reported for several of these components in a
recent paper.[2] The phenyl thiobenzoate
derivatives, 1SP3 and 1SY3, have substantially
higher clearpoint and about the same melting point
as their corresponding phenyl benzoates, 1-P3 and
1-Y3. These thiobenzoates also have higher Δn and
more positive $\Delta \epsilon$ values than the benzoates.[2] The
two o-substituted phenyl benzoates of this group,
$1(CH_3)$-Y3 and 1(Br)-Y3, each have a lower melting
point and clearpoint than either 1-P3 or 1-Y3.
The o-substituents also have a large effect on $\Delta \epsilon$,
with $1(CH_3)$-Y3 more positive and 1(Br)-Y3 much
more negative in $\Delta \epsilon$ than the unsubstituted R-YR'
structures.[2] The cyclohexyl benzoate derivatives
1[C]-P3 and 1[C]-Y3 each have a lower melting
point and clearpoint than 1-P3 and 1-Y3. In
general, the replacement of a biphenylcarboxylate
by a cyclohexylbenzoate has little effect on the
nematic range, e.g. each of the following pairs
have similar nematic ranges: 1-P3 and 1-Y3, 20-P3
and 20-Y3, 1[C]-P3 and 1[C]-Y3. However, the
bicyclohexylcarboxylate structures, 1-[C]Y3 and
1[C]-[C]Y3, do have substantially lower melting
points than these other structures.

VISCOSITY OF ESTER LIQUID CRYSTAL COMPONENTS

3.2 <u>Viscosity Measurements and Calculations</u>

The flow viscosity measurements and calculated
results are summarized in Table II. The LC
components are all studied at 25°C as additives to
the RO-R' mixture HRL-2N42, which is a five-
component eutectic mixture[1,2,3] of 10-1, 20-3,
20-5, 40-1, and 40-3. The observed viscosity of
this RO-R' mixture with x mole fraction of the
additive(s) is used to estimate the approximate
viscosity contribution of the additive (n_{calc})
by applying equation 1 at the average molecular
length ($\bar{L}$) of the overall mixture:

$$n_{obs} = n_{calc} (x) + n_{RO-R'} (1-x) \qquad (1)$$

The host viscosity value $n_{RO-R'}$ is assumed to
vary linearily with the $\bar{L}$ of the overall
mixture, as noted previously[1], and the values are
taken from equation 2.

$$n_{RO-R'} = 32.5 + 1.54 (\bar{L}-20) \qquad (2)$$

This provides a small correction for differences
in the molecular lengths of the additive. The
class value of viscosity for each type of
structure is assigned from the n_{calc} values
obtained from components of each class.

The n_{calc} values are extrapolations which
are assumed to correspond to the relative

Table II. Viscosity Measurements and Calculated Component Viscosity[a]

Code	Source[b]	Length (Å)	Mixed In HRL-2N42			η_{calc} (cP)
			%	$\bar{L}$ (Å)	$\eta_{25°}$ (cP)	
1-P3	I	21.45	10	20.50	38.03	81
1SP3	I	21.80	10	20.74	38.20	79
1-Y3	I	22.68	10	20.62	37.05	69
1SY3	I	22.53	10	20.60	36.27	62
1(CH_3)-Y3	I	22.68	25	20.96	61.56	144
1(Br)-Y3	I	22.68	25	20.96	76.04	202
1[C]-P3	I	21.60	10	20.51	39.00	90
1[C]-Y3	I	21.30	10	20.48	37.62	77
1-[C]Y3	I	22.20	10	20.57	31.61	16
1[C]-[C]Y3	I	22.50	10	20.60	31.96	19
2-Y3	I	24.28	25	21.40	41.99 [c]	54
2-Y5	I	25.50	25	21.48	42.72	67
4-Y3	I	25.52				
4-OOCY4	I	28.74	25	22.48	50.01	91
20-P3	I	23.60	10	20.86	40.64 [d]	102
20-P5	I	26.10				
20-Y3	I	23.70	25	21.60	49.68 [e]	94
20-Y5	I	26.18				
[Py]-PO5	I	23.65	10	20.72	49.72	195
[Py]-[C]Y3	I	20.50	10	20.40	36.83	37
3[C]-Y2	M	23.45	25	21.47	47.57 [f]	86
3[C]-Y4	M	25.75				
3[C]-[C]Y4	M	24.90	10	20.84	32.54	21
3Y-[C]4	M	25.65	10	20.92	33.75	32
4(CN)-Y3	M	25.52	10	20.90	48.19	177
5-[C]5	A	25.00	10	20.85	29.48	~9
20S[C]5	A	22.80	25	20.99	30.63	20
50S[C]4	A	25.80	25	21.74	35.18	35
NC-[C]5	A	21.85	25	20.76	38.69	54

[a] Extrapolated viscosity from effect of component when added to the RO-R' mixture HRL-2N42. [b] I= Table I in this paper, M= E. Merck, A= Atomergic Chemetals. [c] First mixture with 11.2% 2-Y3 and 13.8% 4-Y3; second mixture with 7.8% 2-Y3, 7.9% 2-Y5, and 9.4% 4-Y3. [d] Mixture with 3.9% 20-P3 and 6.1% 20-P5. [e] Mixture with 9.8% 20-Y3 and 15.2% 20-Y5. [f] Mixture with 11.2% 3[C]-Y2 and 13.8% 3[C]-Y4.

viscosity values of the additives at $25^{\circ}C$ in the environment of the RO-R' host. Our comparisons are made assuming that each additive is accommodated by (or disrupts) the LC host similarly. Of course this is not strictly true, as is obvious, for example, in the case of the additive 5-[C]5 which gives a negative η_{calc} value. Nevertheless, we find that the η_{class} values assigned from these η_{calc} values (and from prior studies) give fairly accurate predictions for the $\eta_{25^{\circ}C}$ of many multicomponent ester mixtures.[1,2] Thus, the η_{class} values are suitable for relative comparisons of LC structural effects on the flow viscosity.
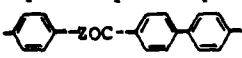
3.3 Effects of Cyclohexane Rings

Table III shows the effects on the extrapolated component viscosity of replacing from one to three of the phenyl groups in 1-P3 with cyclohexyl groups, and of replacing one phenyl group in 1SP3 with a cyclohexyl ring. Each component in Table III has three rings in the same arrangement and has the same alkyl end groups, so that the only structural variation for each ester or thioester is the number and the position of the cyclohexyl groups. The clearpoint of these ester components vary between 126 and $204^{\circ}C$, but since only 10% of each is used in the HRL-2N42 the clearpoints of the mixtures which are used for the

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viscosity measurements are not significantly
different. The structural effects on viscosity in
this series are apparent. The replacement of
phenyl by cyclohexyl on the "alcohol" side of the
ester linkage increases the viscosity:
e.g. 1[C]-P3 > 1-P3, 1[C]-Y3 > 1-Y3, and
1[C]-[C]Y3 > 1-[C]Y3. The substitution of a
cyclohexyl ring for the outside phenyl ring on the
biphenylcarboxylate side decreases the viscosity:
e.g. 1-Y3 < 1-P3, and 1[C]-Y3 < 1[C]-P3. The
thioester structure shows a similar effect, e.g.
the viscosity of 1SY3 < 1SP3. However, these
effects are relatively small compared to the large
decrease in η_{calc} resulting by replacement of
both phenyls on the biphenylcarboxylate side with
cyclohexyl rings: e.g. 1-[C]Y3 << 1-P3(and 1-Y3),
and 1[C]-[C]Y3 << 1[C]-P3 (and 1[C]-Y3).

Table III. Effect on Calculated Component Viscosity of Substituting
Cyclohexyl For Phenyl Groups in 1-P3 and 1SP3.

Compound Code	Number of Cyclohexyls	Replacement Position of Cyclohexyl Groups			$\eta_{calc.}$ (cP, 25°C)
1-P3	0	---	---	---	81
1SP3	0	---	---	---	79
1[C]-P3	1	X	---	---	90
1-Y3	1	---	---	X	69
1SY3	1	---	---	X	62
1[C]-Y3	2	X	---	X	77
1-[C]Y3	2	---	X	X	16
1[C]-[C]Y3	3	X	X	X	19

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The comparisons in Figure 1 confirm that there is in general a substantial decrease in class viscosity when a phenyl ring adjacent to ester carbonyl ("acid" side) is replaced by a cyclohexyl ring, e.g. when a benzoate group is

—OOC—⟨phenyl⟩— GROUP		—OOC—⟨H⟩— GROUP	
CLASS STRUCTURE	η_{CLASS}	CLASS STRUCTURE	η_{CLASS}
R—⟨⟩—OOC—⟨⟩—OOC—⟨⟩—R'	130	R—⟨⟩—OOC—⟨⟩—OOC—⟨H⟩—R'	91
NC—⟨⟩—OOC—⟨⟩—R'	82	NC—⟨⟩—OOC—⟨H⟩—R'	54
R—⟨H⟩—OOC—⟨⟩⟨H⟩—R'	82	R—⟨H⟩—OOC—⟨H⟩⟨H⟩—R'	20
R—⟨⟩—OOC—⟨⟩⟨H⟩—R'	67	R—⟨⟩—OOC—⟨H⟩⟨H⟩—R'	16
RO—⟨⟩—SOC—⟨⟩—R'	37	RO—⟨⟩—SOC—⟨H⟩—R'	27
RO—⟨⟩—OOC—⟨⟩—R'	36	RO—⟨⟩—OOC—⟨H⟩—R'	16
R—⟨⟩—OOC—⟨⟩—R'	19	R—⟨⟩—OOC—⟨H⟩—R'	(0)

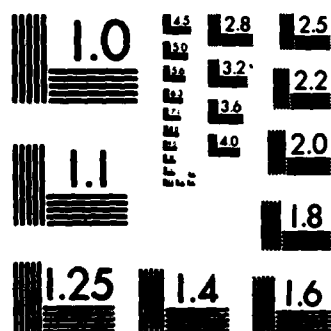FIGURE 1 Effect on class viscosity of replacing a benzoate group with a cyclohexane-carboxylate group.

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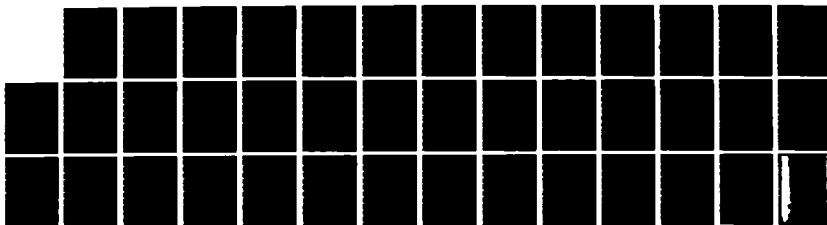
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

replaced by a cyclohexanecarboxylate group. A similar, but smaller decrease in η_{class} occurs in thio-ester structures: e.g. ROS[C]R' < ROSR'. Even when only one benzoate group is replaced in a diester structure, a large viscosity decrease is shown: e.g. R-OOCYR' < R-OOCPR'. Quite low η_{class} values are observed for the R-[C]YR', RO-[C]R', and R-[C]R' cyclohexane-carboxylate structures, each of whose LC compounds also have the advantage of having higher clearpoints than the corresponding benzoate compounds.

The effects on η_{class} of replacing a phenyl ester with a cyclohexyl ester are summarized in Figure 2. The η_{class} increases by an average of
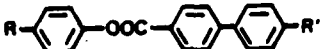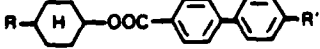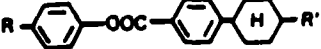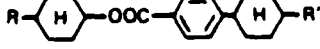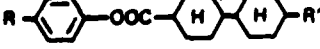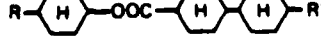

FIGURE 2 Effect on class viscosity of replacing phenyl ester with a cyclohexyl ester.

about 20% when cyclohexyl replaces phenyl on the "alcohol" side of these structures.

The effects of replacing a biphenylcarboxylate group with a cyclohexylbenzoate group are summarized by the η_{class} comparisons in Figure 3. On the average this structural change decreases η_{class} by about 13%.

3.4 Effects of Ortho-Groups

The use of ortho-groups in LC structures is of
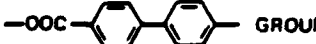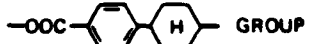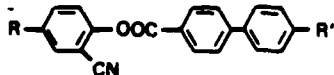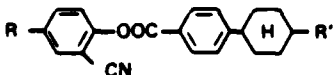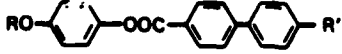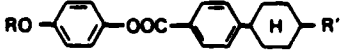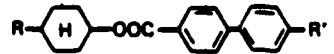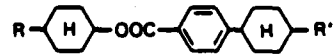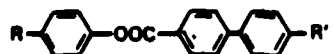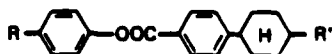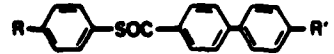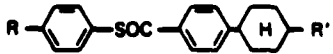
—OOC⟨⟩⟨⟩— GROUP		—OOC⟨⟩⟨H⟩— GROUP	
CLASS STRUCTURE	η_{CLASS}	CLASS STRUCTURE	η_{CLASS}
R⟨⟩(CN)—OOC⟨⟩⟨⟩—R′	200	R⟨⟩(CN)—OOC⟨⟩⟨H⟩—R′	177
RO⟨⟩—OOC⟨⟩⟨⟩—R′	102	RO⟨⟩—OOC⟨⟩⟨H⟩—R′	94
R⟨H⟩—OOC⟨⟩⟨⟩—R′	90	R⟨H⟩—OOC⟨⟩⟨H⟩—R′	82
R⟨⟩—OOC⟨⟩⟨⟩—R′	81	R⟨⟩—OOC⟨⟩⟨H⟩—R′	67
R⟨⟩—SOC⟨⟩⟨⟩—R′	79	R⟨⟩—SOC⟨⟩⟨H⟩—R′	62

FIGURE 3   Effect on class viscosity of replacing a biphenylcarboxylate with a cyclohexylbenzoate group.

interest mainly as a means of altering the $\Delta\varepsilon$ and lowering the mp compared to the structure without the o-group. Among the o-groups whose viscosity effects are studied here, the o-Br, o-pyridyl, and o-CN groups give an increasingly strong negative $\Delta\varepsilon$ effect to their parent phenyl ester LC structures, while the o-CH$_3$ group increases the positive $\Delta\varepsilon$ of its parent structure.[2] However, one price paid for the lower mp and the altered $\Delta\varepsilon$ is that of a substantial increase in η_{class} of the o-group structures, as shown in Figure 4. The addition of an o-CN or o-Br group greatly increases the viscosity of a structure, generally more than doubling the η_{class}, while the presence of an o-pyridyl group causes a smaller viscosity increase. The addition of an o-CH$_3$ group strongly increases η_{class}, while an o-Cl group causes a smaller increase. In general the results shown in Figure 4 indicate that the increase of η_{class} due to the presence of o-groups is in approximately the following order: Br > CN > CH$_3$ > pyridyl > Cl.

4. CONCLUSIONS

1. The replacement of phenyl rings by cyclohexyl rings in ester LC compounds alters their relative value of class viscosity, with the magnitude and the direction of the effect strongly

VISCOSITY OF ESTER LIQUID CRYSTAL COMPONENTS

WITHOUT o-GROUP		WITH o-GROUP	
CLASS STRUCTURE	η CLASS	CLASS STRUCTURE	η CLASS
R—⬡—OOC—⬡—⬡—OR′	160	R—⬡(CN)—OOC—⬡—⬡—OR′	310
		⬡(N)—OOC—⬡—⬡—OR	195
R—⬡—OOC—⬡—OOC—⬡—R′	130	R—⬡—OOC—⬡(Cl)—OOC—⬡—R′	153
R—⬡—OOC—⬡—⬡—R′	81	R—⬡(CN)—OOC—⬡—⬡—R′	200
R—⬡—OOC—⬡—⬡(H)—R′	67	R—⬡(Br)—OOC—⬡—⬡(H)—R′	202
		R—⬡(CN)—OOC—⬡—⬡(H)—R′	177
		R—⬡(CH₃)—OOC—⬡—⬡(H)—R′	144
R—⬡—OOC—⬡(H)—⬡(H)—R′	16	⬡(N)—OOC—⬡(H)—⬡(H)—R′	37

FIGURE 4 Effect on class viscosity of ortho-groups.

dependent upon the position of the cyclohexyl
groups in the structure. When the class
viscosities are extrapolated from viscosity
measurements of the LC compounds as additives in a

standard host mixture of alkoxyphenyl alkylben-
zoates, then for otherwise comparable structures
the effects on η_{class} of replacing a phenyl ring
with a cyclohexyl ring are typically as follows:
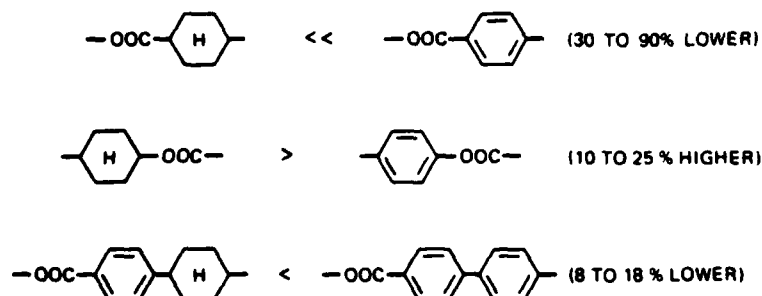
Thus, substitution of a cyclohexyl for a phenyl
ring adjacent to the carbonyl group is by far the
most effective way of using cyclohexyl rings to
reduce the viscosity of ester LC structure.

    2. Although o-groups can be used effectively
to control the dielectric anisotropy contribution
of component structures, and also to lower the
melting point, this advantage is offset by a
substantial increase in the class viscosity of a
structure with an o-group as compared to the
structure without it. In the present studies the
presence of an o-group in a component increases
the η_{class} value in the range of 20 to 200%.
For these structures the magnitude of the o-group
effect on η_{class} increases as follows:
Cl < pyridyl < CH_3 < CN < Br.
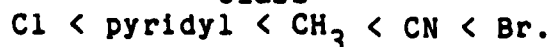
    3. The assignment of class viscosities to LC
ester structures is useful in comparing structural

effects of cyclohexyl rings and o-substituents on the relative viscosity contributions of ester and thioester LC compounds. The twenty n_{class} values assigned here along with the other eighteen assigned earlier,[1] can be used effectively to predict the flow viscosity of new multicomponent LC nematic mixtures.[2,6]

5. ACKNOWLEDGMENTS

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APPENDIX D

IMPROVED MATERIALS FOR DC DYNAMIC SCATTERING AT ELEVATED TEMPERATURES*

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Liquid crystal (LC) mixtures and a sealant
suitable for dc-activated dynamic scattering
(DS) matrix displays are developed for wide
range storage temperature (-60 to 80°C) and
for elevated temperature operation. Three
improved eutectic nematic mixtures are
formulated with nematic ranges (undoped) of 0
to 74, -4 to 82, and -13 to 78°C, with flow
viscosities of 31, 32 and 36 cP respectively.
Several types of sealants are tested in
contact with LC and are evaluated according
to the level of contamination they introduce
at elevated temperature. One UV-curved
sealant shows no apparent degradation effects
after more than 1800 hours of 100°C heating
with an undoped ester LC in a vacuum-filled
test cell made with this sealant. Thermal
storage stability at 80°C and low temperature
stability at -60°C in such sealed cells show
little change in surface alignment,
resistivity, and DS characteristics in LCs
with redox dopants, namely dialkylferrocene
and (2,4,7-trinitro-9-fluorenylidene)-
malononitrile. The LC materials with this
redox dopant also show good thermal stability
for over 1100 hours at 100°C in evacuated
glass ampoules. Elevated temperature dc-DS
stability with 20 V dc at 55°C shows more
than 5000 hours for two of the new redox-
doped LC mixtures in sealed transparent
cells. The viscosity, dielectric anisotropy,
conductivity anisotropy, and dc-activated DS
effects are studied as a function of

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temperature for one of the mixtures.
Response times of DS as a function of
temperature (25° to 65°C) and cell thickness
are also studied.

1. INTRODUCTION

The dynamic scattering (DS) mode is useful for
several types of liquid crystal (LC) display
applications[1], most of which require a wide
temperature range for device storage as well as a
fairly wide operational temperature range for the
LC materials. However, because the DS mode is
dependent upon the anisotropic conduction of ionic
species, the operational range is in general
somewhat limited due to the exponential dependence
of ionic conduction upon temperature. We are
particularly interested in using dc-activated DS
for an active-matrix pictorial LC display with MOS
(metal-oxide-semiconductor) substrate cir-
cuitry[2-5]. The dc-DS mode provides a gray scale
capability for this matrix display, and dc-
activation of the LC picture elements (pixels) is
the simplest way to utilize the MOS circuitry. In
this circuitry a field effect transistor (FET) is
switched open just long enough to charge a pixel
capacitor, which provides the activating voltage
across the LC pixel during each picture frame time
(e.g., 33 ms). The LC must be conductive enough
to give a full level dc-DS response, but must be
resistive enough so that the capacitor remains
sufficiently charged to maintain an adequate
voltage across the LC during the frame time. At

room temperature with a typical LC thickness (e.g., 10 μm) the operational range for the LC resistivity in this MOSFET addressed display is approximately between 10^9 and 10^{10} ohm-cm. The resistivity is strongly temperature dependent for redox doped LC esters[1], with an order of magnitude change between about 25 and 70°C for the ac-resistivity and between about 35 and 71°C for the apparent dc-resistivity for cells activated at 20V.

Although the use of redox dopants[6] permits long lifetimes for the dc-activation of ester LCs, the resistivity of unsealed cells gradually increases over long periods of dc operation, even in nitrogen-flushed ovens.[1,6] On the other hand, cells sealed with epoxy type sealants have shown a very short dc-lifetime at elevated temperatures due to electrochemical effects from ionic impurities introduced into the LC from the sealant material.[1] The present work was initiated with the goal of obtaining improved LCs and sealants compatible with the dc-activation of MOS-addressed matrix displays in the elevated temperature range of about 35 to 71°C. Cells can be readily heated, and operation above room temperature is advantageous for faster response times. In addition, environmental conditions may require operation up to about 71°C in some cases if the cells are not cooled. Our aims were (1) to develop improved redox-doped ester LC mixtures with a wider nematic temperature range, lower

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viscosity, and faster response times, and (2) to
obtain sealants compatible with these LCs and
capable of permitting long life dc-activation of
MOS-addressed matrix cells at elevated
temperatures as well as long term storage at both
high and low temperatures.

2. EXPERIMENTAL

The LC components used in these studies belong to
the structural classes shown in Figure 1. The
class code nomenclature is similar to ones we have
used previously.[1,7-11] For specific compounds the
R and R' end groups are identified numerically by
the number of carbon atoms in their n-alkyl end
groups, e.g., 20-3 refers to p-ethoxyphenyl p-n-
propylbenzoate. The synthesis or source of the
individual compounds is given in the Figure 1
references. The LC purity and properties are
measured as described previously.[1,7-10] For DS
studies "redox dopants" were added, generally 0.5%
each of a dialkylferrocene and (2,4,7-trinitro-9-
fluorenylidene)malononitrile (TFM). Either
dibutylferrocene (DBF) or dihexylferrocene (DHF)
are used. The DBF is used in HRL-26N4 and -26N25,
and the DHF in HRL-26N35 and -26N36. The TFM and
DBF were purified commercial products, while the
DHF was synthesized by acylation of ferrocene with
hexanoyl chloride to give dihexanoylferrocene,
which was then reduced to DHF and purified. The
DS measurements are made in the same manner as
before,[1,7,8,12] namely in transmission at normal

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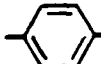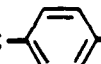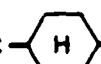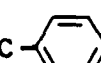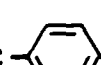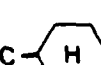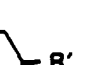
STRUCTURE CLASS	CLASS CODE	REFERENCES
RO—⬡—OOC—⬡—R'	RO–R'	1, 7
RO—⬡—OOC—⬡—OR'	RO–OR'	1, 9
RO—⬡—OOC—⬡—OOCR'	RO–OOCR'	1, 9
RO—⬡—OOC—〈H〉—R'	RO–[C] R'	1, 8
R—⬡—OOC—⬡—OOC—⬡—R'	R–OOCPR'	9, 10
R—⬡—OOC—⬡—OOC—〈H〉—R'	R–OOCYR'	10, 11
R—⬡—OOC—⬡〈H〉—R'	R–YR'	10

FIGURE 1   Structure and code symbols for classes
of LC ester components used in these
studies.

incidence using unpolarized, collimated green
light centered at 525 nm, with a detector
acceptance angle of about $\pm 2^{\circ}$. The DS response
times are measured in unsealed cells made from
optical flats with several hard SiO_x spacer pads
deposited near the perimeter. The thickness of

these empty cells are measured by a standard
interferometer technique with a Cary 14
spectrophotometer. The LC in both sealed and
unsealed cells are surface-parallel aligned, by
rubbing the spin coated and oven-baked polyvinyl
alcohol (PVA), as before,[1] on indium-tin oxide
(ITO) transparent electrodes on float glass. The
LC ac-resistivity is normally measured at 100Hz
with 0.1V rms in cells with surface-parallel
alignment, although some nominal dc-resistivity
values are shown at 55°C and 20V dc while the LC
is undergoing DS. The materials used for sealing
tests are identified by their manufacturer's code,
and the sealing (curing) conditions are those
recommended by these suppliers.

3. RESULTS AND DISCUSSION

3.1 New LC Mixtures: Composition and Properties

The compositions of the three new ester mixtures
HRL-26N25, -26N35, and -26N36 are given in Table I
along with that of HRL-26N4. The latter is shown
for comparison purposes, since it was one of the
better mixtures that we studied previously for use
at elevated temperatures.[1] The techniques of
formulating these new mixtures were described
recently:[10] The components were selected to give
mixtures with a wider nematic range (especially a
lower melting point), a lower viscosity, and a

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TABLE I. Composition of Liquid Crystal Eutectic Mixtures.

Component	Mole Fraction of Components in HRL Mixtures			
Component Code	26N4	26N25	26N35	26N36
20-3	0.108	0.061	0.054	0.057
20-5	0.120	0.057	0.058	0.062
40-1	-----	-----	0.037	0.039
40-3	-----	-----	0.034	0.036
40-6	-----	-----	-----	0.110
60-5	-----	0.229	0.204	0.214
60-01	0.194	-----	-----	-----
10-00C3	0.058	0.037	0.032	-----
40-00C4	0.073	0.045	-----	-----
60-00C5	0.223	-----	-----	-----
10-[C]5	-----	0.272	0.245	0.256
20-[C]3	0.222	0.142	0.124	-----
20-[C]5	-----	0.077	0.066	0.070
4-00CY4	-----	-----	0.059	-----
4-00CP4	-----	0.070	-----	0.065
3-Y3	-----	-----	0.087	0.091

less negative dielectric anisotropy than HRL-26N4.
These changes were accomplished primarily by
replacing the RO-OR' component and one or more of
the RO-OOCR' components with more structures

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containing cyclohexyl groups, such as RO-LCJR',
R-YR', and R-OOCYR'. The resultant properties of
the undoped mixtures are shown in Table II, and
these are in fairly good agreement with the
calculated values predicted[10] for melting point,
clearpoint, birefringence (Δn), viscosity (η), and
dielectric anisotropy ($\Delta\varepsilon$). The conductivity
anisotropy ($\sigma_\parallel/\sigma_\perp$) was measured after doping the
mixtures with 0.5% each of a dialkylferrocene and
TFM, and then filtering the LC to remove any
undissolved particles. Typical dc-DS curves of
percent scattering (%S) versus voltage are shown
in Figure 2 for these four mixtures. Tne
HRL-26N36 mixture has the best scattering
characteristics of the three new mixtures, and it
is the one most comparable to HRL-26N4. The
superimposition of a high frequency bias signal (5
or 10V of 10kHz) shifted the dc-DS curves of
HRL-26N36 considerably toward higher threshold
voltages and steeper %S changes just above
threshold. However, these high frequency bias
signals had a small effect on the DS response
times at 20V dc; for example, a cell of 11.3 μm
thickness showed on-times of 18, 26, and 25 ms and
decay times of 132, 140 and 123 ms respectively
for 10 kHz bias voltages of 0, 5, and 10 V rms.

3.2 Elevated Temperature Effects on LC Properties
The data in Figures 3, 4, and 5 show the effects
of elevated temperature on several important LC
properties, comparing HRL-26N36 with HRL-26N4.

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TABLE II. Properties of LC Mixtures

Property[a]	Mixture HRL Number			
	26N4	26N25	26N35	26N36
Melting Point, °C	21	0	-4	-13
Clearpoint, °C	77.0	73.9	81.9	77.6
Average Length, Å	23.3	23.2	23.0	23.8
Δn at 23°C	0.14	0.12	0.12	0.13
η at 25°C, cP	49	31	32	36
$\Delta\epsilon$ at 25°C[a]	-0.96	-0.57	-0.70	-0.28
$\epsilon_\perp$ at 25°C[a]	6.15	5.04	4.85	4.84
$\sigma_\parallel/\sigma_\perp$ at 25°[b]	1.40	1.44	1.56	1.42

[a]
 Measured at 500 Hz
[b]
 Measured at 100 Hz with 0.5% redox dopant

The temperature effect on the ac-resistivity $(\rho_\perp)$
of the redox-doped mixtures is similar to the
temperature effect on the flow viscosity of the
undoped mixtures, as illustrated by the $\rho_\perp$ and η
comparisons shown in Figure 3. Both viscosity and
resistivity show a similar exponential dependence
on T^{-1}, with their log plots showing similar
deviation from linearity at higher temperatures.
The effect of temperature on the conductivity
anisotropy of redox-doped HRL-26N36 is similar to

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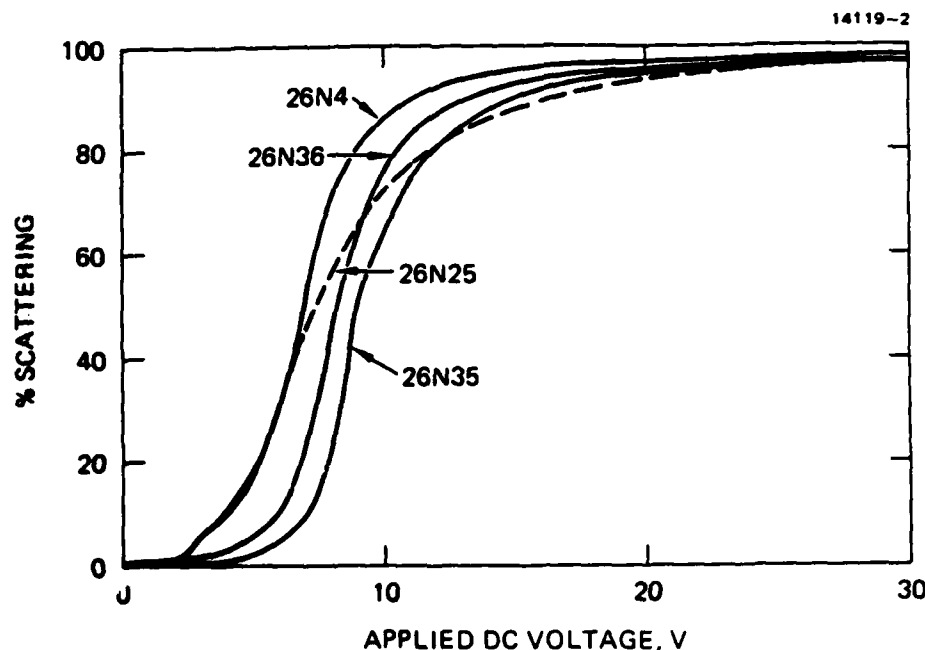
FIGURE 2   DS curves, 12 μm thick cells of
            optical flats/ITO/PVA (rubbed), 23°C.

that of HRL-26N4, as shown by the comparisons in
Figure 4.   The $\sigma_\parallel/\sigma_\perp$ of HRL-26N36 is higher at all
temperatures, and it is above 1.3 even at 70°C due
to the relatively high clearpoint of this mixture.
The temperature effects on the dielectric
anisotropy and dielectric constant of these two
mixtures are compared in Figure 5.   As indicated
in Table II, the $\Delta\varepsilon$ values for HRL-26N25 and -
26N35 are intermediate between those of
HRL-26N4 and -26N36.

    Temperature and cell thickness effects on the
scattering versus voltage curves for the dc-DS of
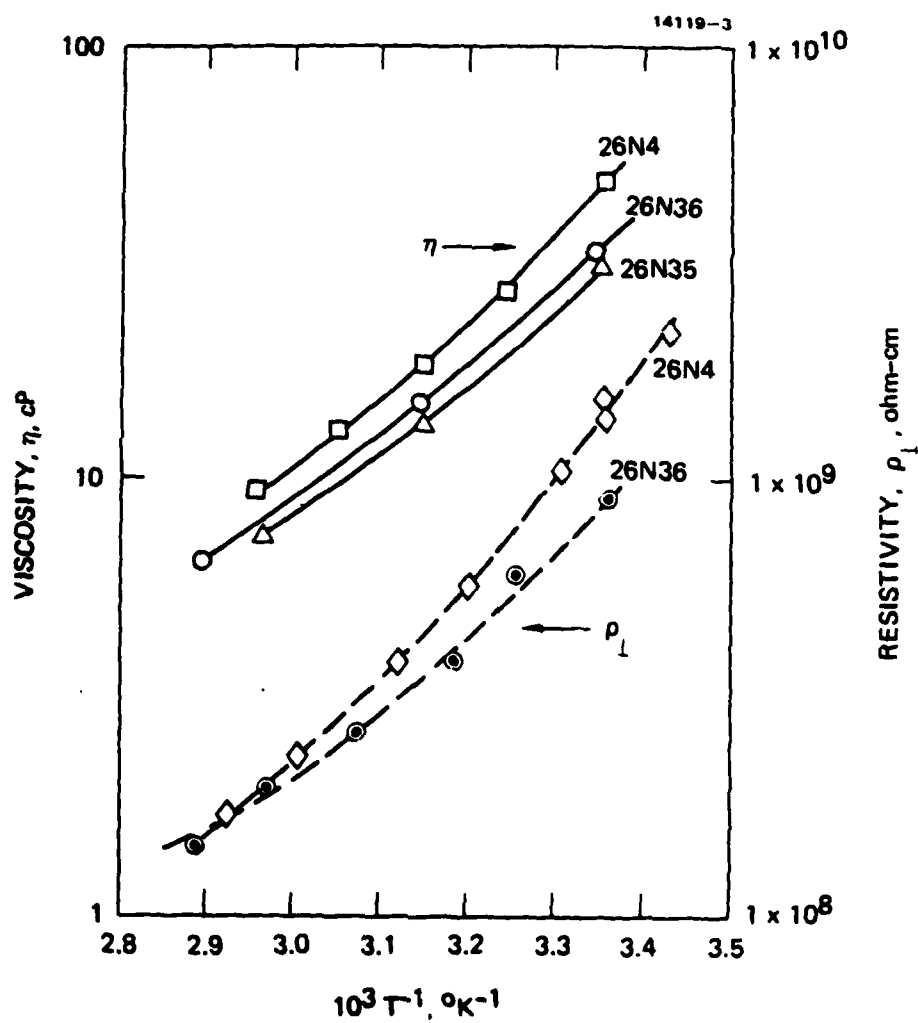
FIGURE 3   Effect of temperature on flow viscosity
and ac-resistivity

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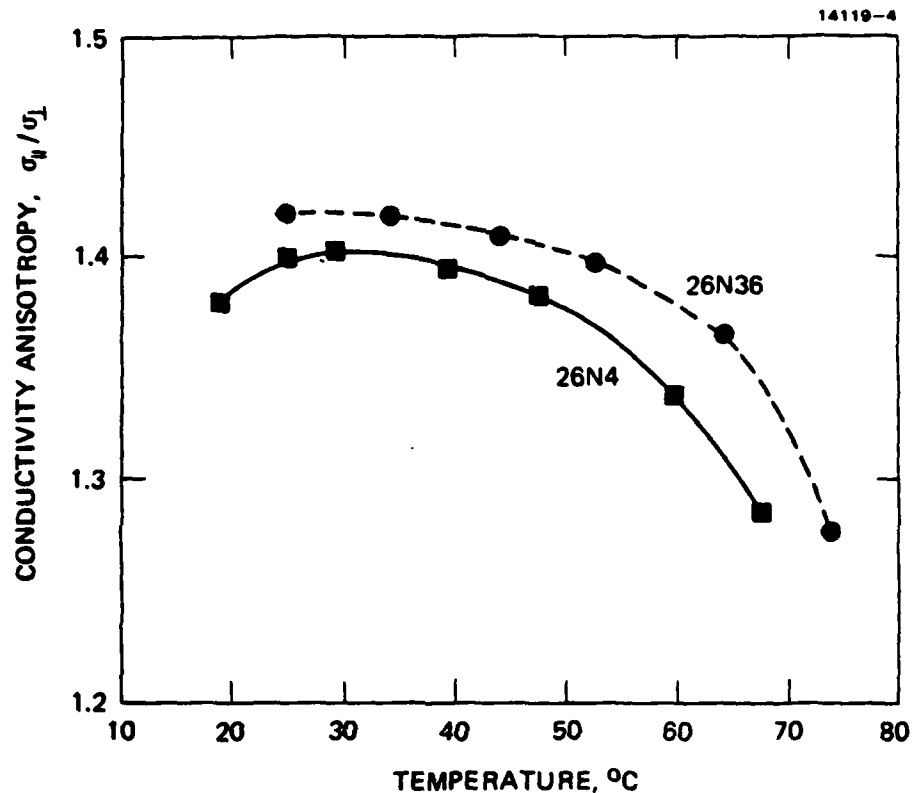
FIGURE 4   Effect of temperature on conductivity
            anisotropy.

HRL-26N36 are shown in Figure 6. In contrast to
our observations that ac-DS is more efficient in
thinner cells,[12] the scattering for dc-DS is not
as high in cells of 6 μm as compared to 12 μm
thickness. At higher temperatures (e.g., 60-65°C
in Fig. 6) the scattering efficiency peaks at a
lower voltage (10 to 12 V dc) and the %S falls off

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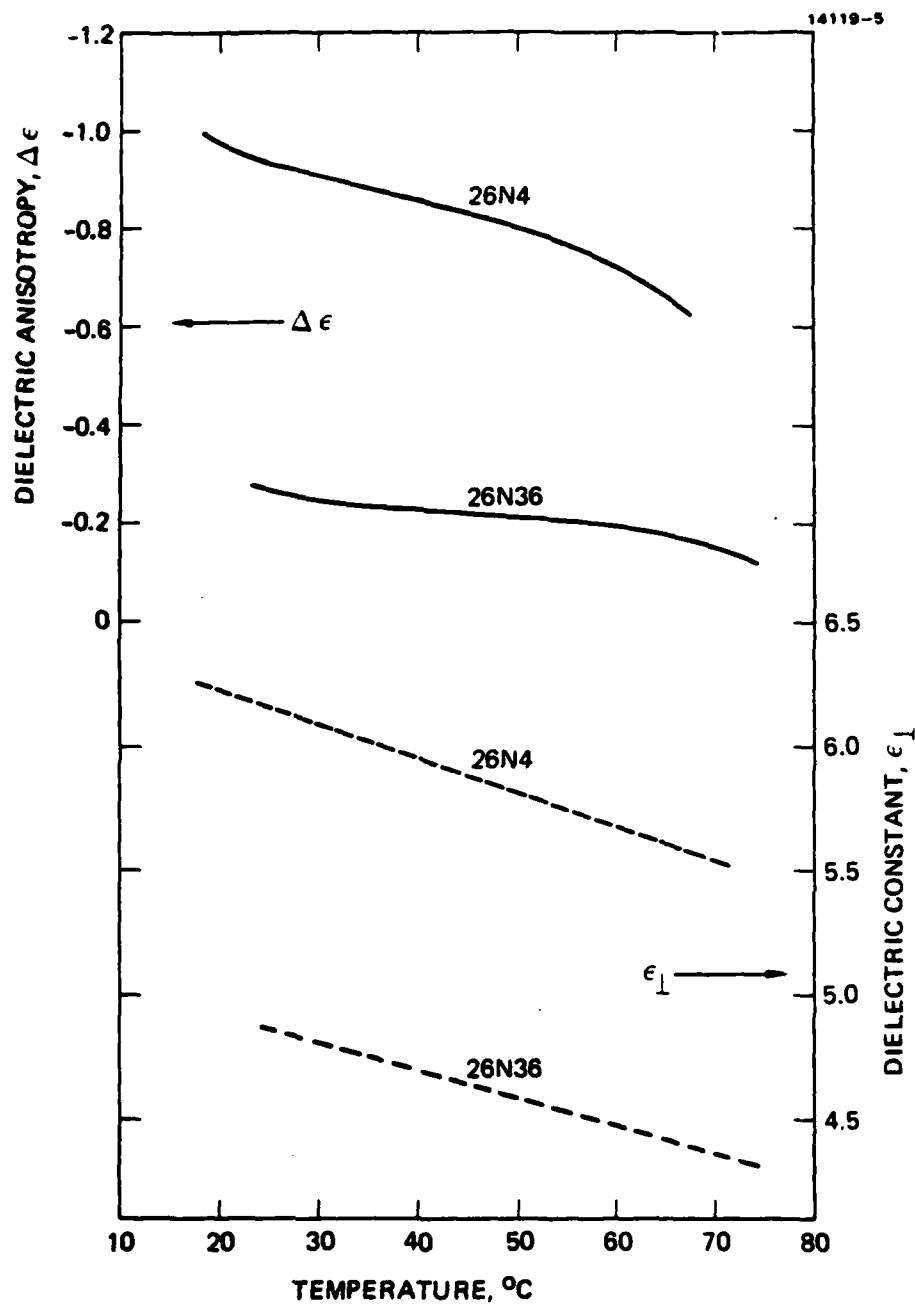
FIGURE 5   Effect of temperature on dielectric
anisotropy and dielectric constant.
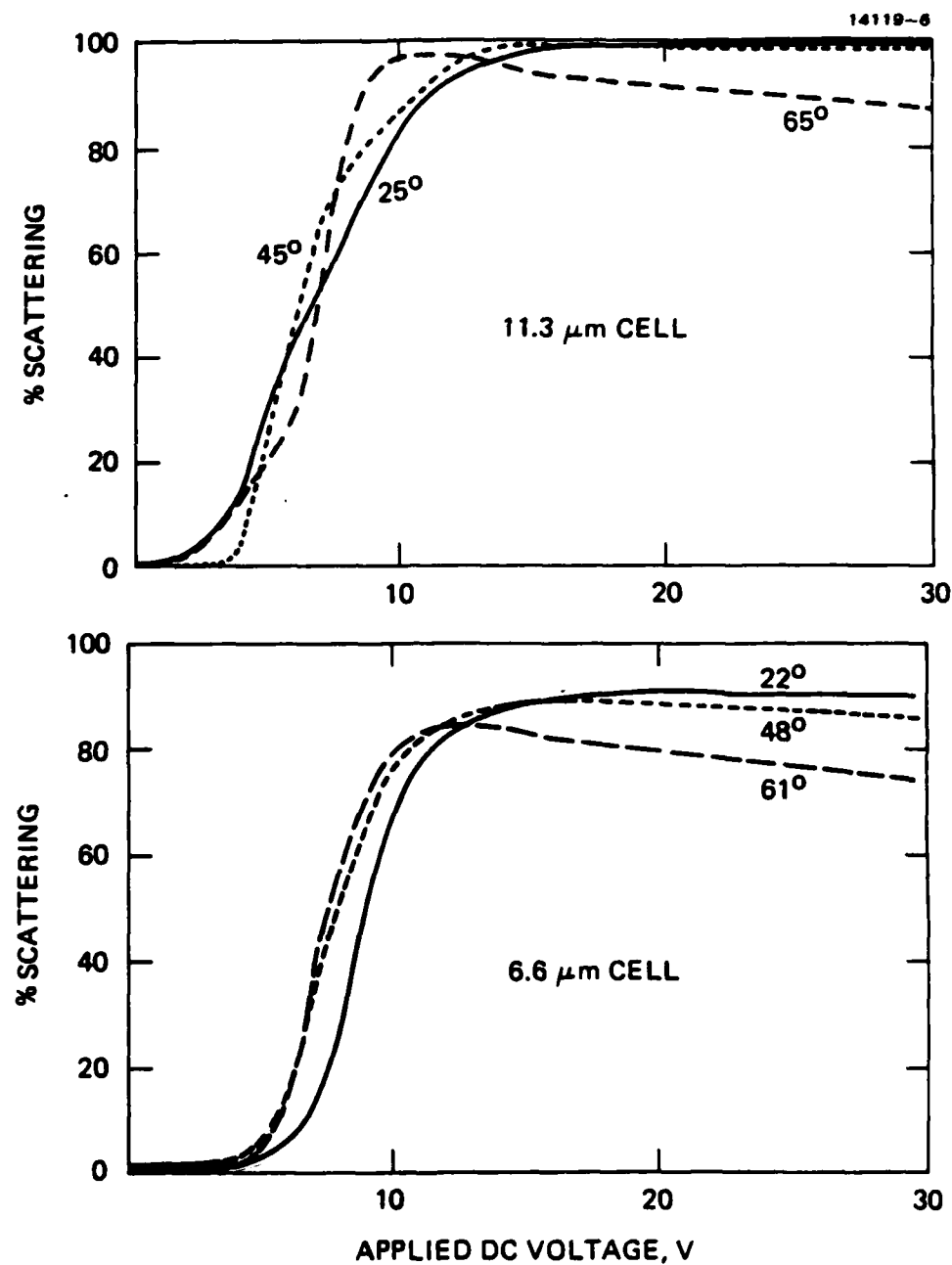
FIGURE 6   Effect of temperature and cell
thickness on scattering curves for
dc-DS.

at higher voltages. This higher voltage decrease in the dc-DS efficiency is more prominent at higher temperatures, in thinner cells, and in samples of lower resistivity. Because all of these factors cause higher current levels in the cells, we speculate that this higher voltage fall off of %S is related to a space charge build up at the PVA-coated electrodes.

The effects of elevated temperature and cell thickness on the DS response times of HRL-26N36 at 20 V dc are illustrated by the typical values shown in Figure 7, where the voltage is applied repetitively at 500 ms on and 500 ms off. In the highest temperature region the decay time increases with increased temperature, instead of decreasing as might be expected from the lower viscosity at higher temperatures. (We had observed the same effect previously[1] with other LC mixtures such as HRL-26N4.) Shorter length 20V pulses (e.g., 20 to 100 ms), or lower voltage pulses (e.g., 12 V), give higher %S and considerably faster decay times (e.g., 12 ms at 61°C in a 6 μm thick cell) for HRL-26N36 than the 500 ms voltage pulses of 20V. This is consistant with the idea that at high current levels a space charge build up may be formed that both limits the %S level and increases the decay time.

The response times shown in Figure 7 are equivalent to those previously observed for HRL-26N4, despite the fact that HRL-26N36 has a substantially lower viscosity. Nevertheless, the

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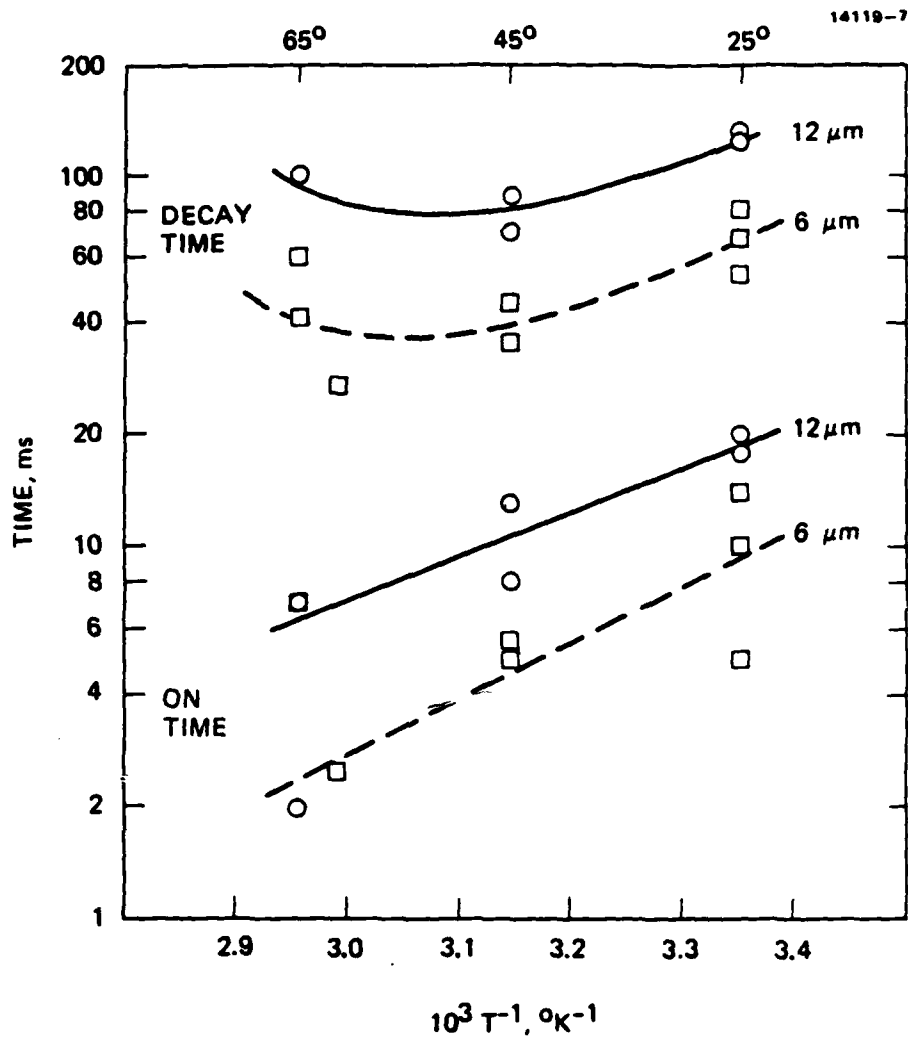
FIGURE 7   Effect of temperature and cell
            thickness on dc-DS response times
            at 20 Vdc.

fast turn on times at high temperature (e.g., 2 to
6 ms at 65°C in Fig. 7) are a small fraction of a
typical 33 ms frame time for a pixel display.

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This indicates that a high scattering level can be
reached in a MOSFET matrix LCD even if the
activating voltage on a pixel decreases during the
frame time at high temperatures due to charge
leakage from the pixel capacitor through the LC.
For example, although the lowest resistivity
sample used in Figure 7 had $\rho_\perp = 2 \times 10^8$ ohm-cm at
65°C, which is only one-fifth of the nominal
resistivity of 10^9 ohm-cm required to maintain
pixel charge at room temperature for 33 ms, the on
time at 20 V and 65°C is less than one-fifth of
this frame time period. In addition, because the
%S is maximum in the 10 to 12 V range (see Figure
6), the effect of any capacitor charge leakage
will be minimal until the voltage drops below 10
V. Thus, a full level scattering should be
reached in a MOSFET matrix display at elevated
temperatures and the average %S level during the
frame time will depend primarily upon the decay
time in the presence of residual charge on the
pixel capacitor.

3.3 Sealant Thermal Stability Studies

A survey test was made on the compatibility of
various sealant materials with an ester LC mixture
at 100°C. A small sample of each sealant was
individually cured in separate aluminum foil pans
(DSC pans), then some undoped HRL-2N52 ester LC
mixture[1] was added, a top was crimped onto each

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pan, and they were heated at $100^{\circ}C$ for 120h in an oven. The LC was examined afterwards by placing it in a 13 μm thick cell with ITO electrodes and testing its resistivity and any impurity-induced DS at 20 V dc. The results are given in Table III, where a pick up of impurities by the LC from the previously cured sealant is shown by a lowering of the LC resistivity and by the presence of ionic impurities causing DS at 20 V dc. Because long life dc-DS operation requires the use of electrochemically reversible dopants, such as the HRL redox dopants, the presence of uncontrolled ionic impurities from the sealant is undesirable--and in fact their presence has been shown to cause very short dc-DS lifetime.[1] Of the fifteen different adhesives surveyed by the Table III tests, five (Nos. 2, 3, 4, 5 and 6) showed relatively little contamination and two others (Nos. 7 and 8) showed slight impurity contamination. We chose sealant Nos. 2 to 8 for further studies, and did not make further studies on the eight additional epoxies (Nos. 9 through 16) in Table III. The No. 8 sealant (Ablefilm 539 -Type II) was included mainly for reference purpose since we already knew that it introduces undesirable impurity dopants into the LC at elevated temperatures.[1]

Additional studies of the seven selected sealants were made in LC test cells with float glass/ITO/PVA substrates using 12.7 μm thick Mylar

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TABLE III. Sealant Compatibility Test: Effect on Undoped
HRL-2N52 LC After 120 Hours at 100°C.

Sealant	Cure Temp. °C	Cure Time Hours	LC Resistivity ohm-cm	DS Due to Sealant Impurities
1. None	----	----	7.87×10^{11}	None
2. Polypropylene[a]	180	0.25	7.87×10^{11}	None
3. Torr seal[b]			1.51×10^{11}	None
4. TPA-84-HP[c]	145	1.5	1.46×10^{11}	None
5. TPA-61	190	0.25	1.41×10^{11}	None
6. Norland NOA-61[d] (UV)	23	0.5	2.62×10^{11}	Slight
7. Lens Bond M62[e]	70	1.0	5.62×10^{10}	Slight
8. Ablefilm 539-Type II[f]	140	1.5	7.15×10^{10}	Little
9. Able Bond 642-1[f]	100	1.0	5.25×10^{10}	Strong
10. Able Bond 681-14[f]	175	1.0	5.25×10^{10}	Strong
11. Lixon 1004 A/B[g]	100	2.0	4.04×10^{10}	Strong
12. Transene Epoxy[h] 50-30-2	100	1.0	4.89×10^{9}	Strong
13. Transene Epoxy 15[h]	100	1.0	1.71×10^{9}	Strong
14. Transene Epoxy 13[h]	100	1.0	1.71×10^{9}	Strong
15. Able Bond 342-13ACC[f]	70	2.0	4.25×10^{9}	Strong
16. Devcon 5 Min Epoxy[i]	70	2.0	2.30×10^{8}	Strong

[a] Transparent Products
[b] Varian Associates
[c] ALX
[d] Norland Products
[e] Summers Laboratories
[f] Able Stik Labs
[g] Hitachi Ltd.
[h] Transene Co.
[i] Devcon Corp.

perimeter spacers. The cells were presealed
except for a small filling hole for the LC. These
cells were evacuated, back-filled with undoped
HRL-2N52, and the filling hole was plugged with
indium metal and overcoated with TPA-61 epoxy.
The cells were heated at 100°C in an oven and
examined periodically at room temperature for
their resistivity and uniformity of alignment.
The results are shown in Figure 8, where the
apparent resistivity (assuming a nominal 12.7 μm
thickness) is plotted and the first change in
surface alignment is noted. During comparable
heating times the cell with Norland NOA-61 sealant
maintained a much higher resistivity (by one to
two orders of magnitude) than the other sealants
tested. It also showed a much longer heating time
before any surface misalignment was observed.
Even after 1836h of 100°C heating the misalignment
in the Norland NOA-61 cell occurred around the
filling hole, which had by then become unplugged.
Because it was far superior to the other sealants
in this test, Norland NOA-61 was chosen for dc-DS
lifetime studies of the improved LC mixture in
sealed cells.

The effect of moisture on the degradation of
the Norland NOA-61 sealant was evaluated by
testing one set of sealed cells immersed in water
and another set in an atmosphere of 75% relative
humidity. The results are shown in Figure 9, from
which the activation energy of this sealant's
degradation is found to be about 12 kcal/mole from

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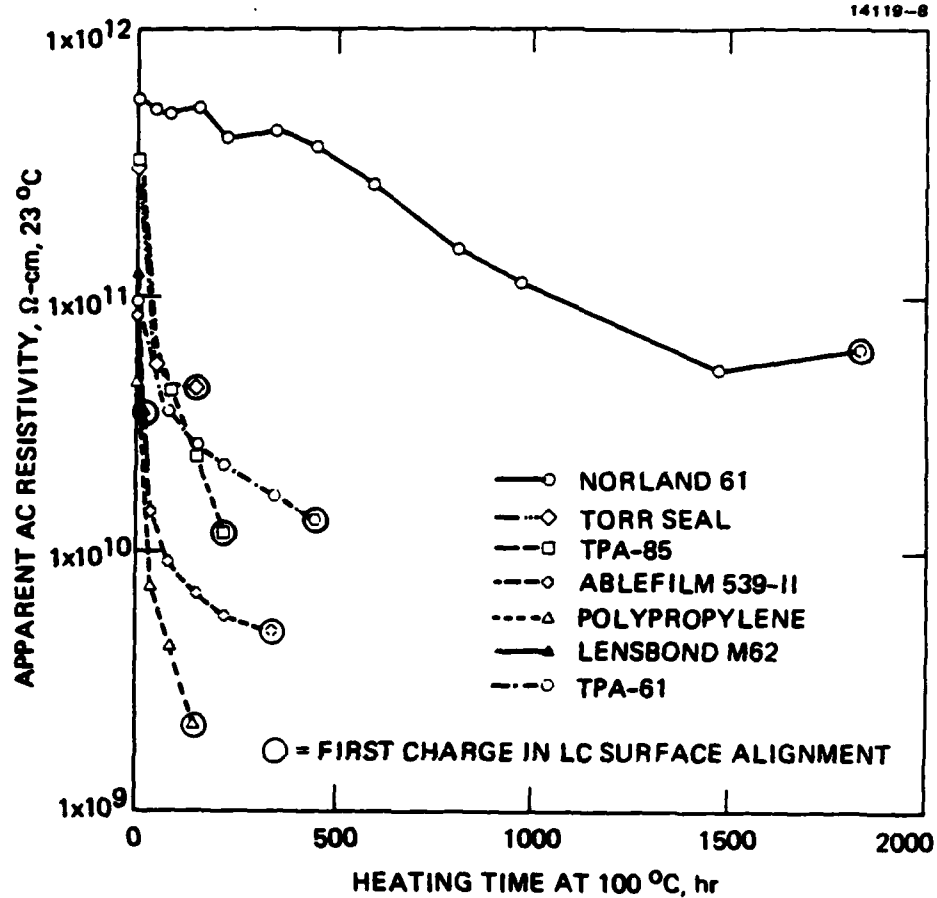
FIGURE 8   Sealant effects on resistivity and
surface alignment of LC cells.

attack by both water and water vapor.   These tests
were made with a perimeter seal, using empty cells
with a Mylar spacer.   Evidence for sealant
degradation was taken as the first noticable
change in the adherence of the outside edge of the
sealant strip, from visual examination on a light
table.   The relative rates of degradation and the
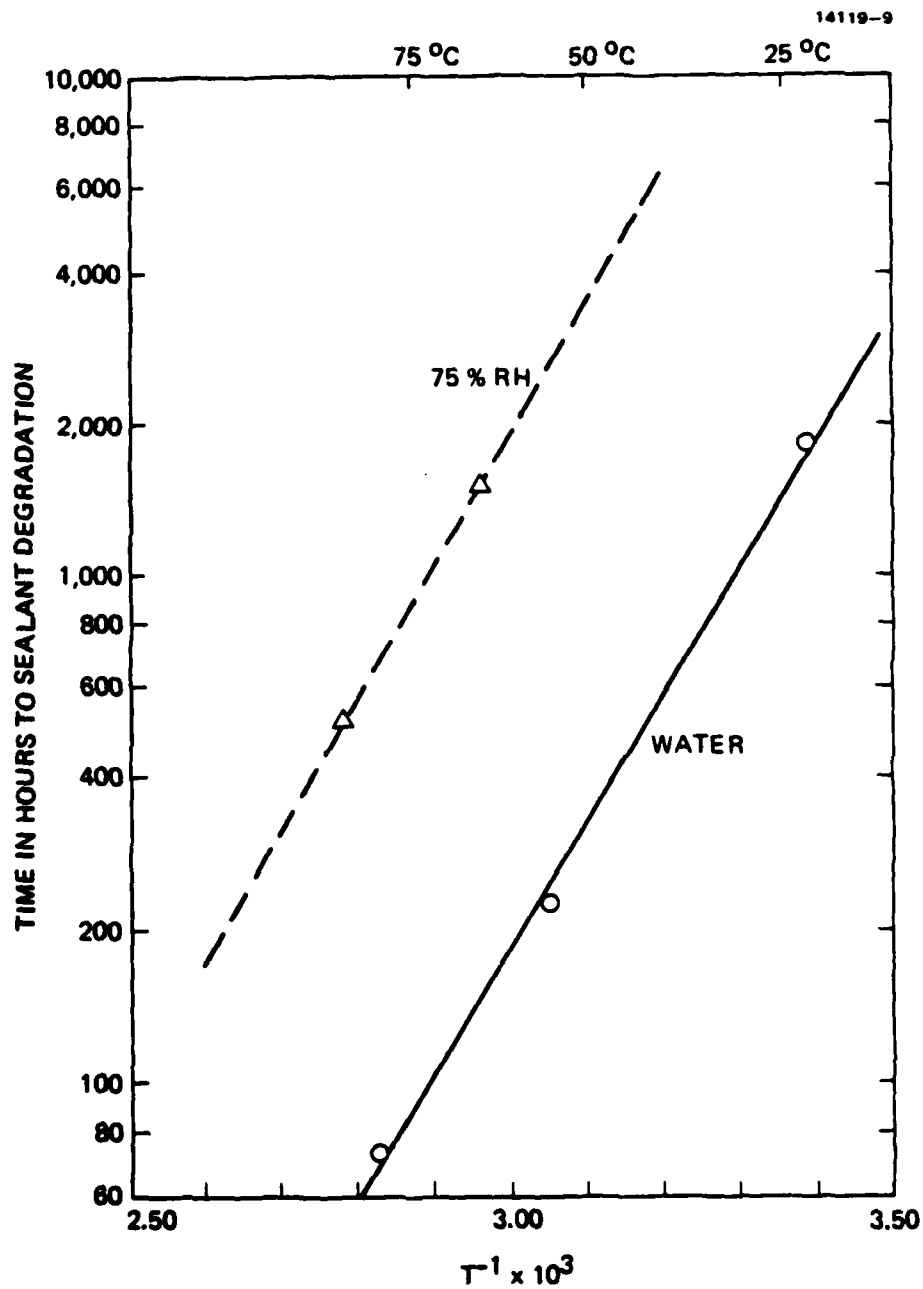
FIGURE 9   Rate of moisture degradation of
            sealant.

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activation energy are the important information gained from the Figure 9 data. Immersion in hot water was chosen as the first accelerated test condition, and the water vapor test results confirm that the activation energy for moisture attack is approximately 12 kcal/mole. This corresponds to sealant degradation times of about 16,500h and 1100h at 25° and $71^\circ C$, respectively, for Norland NOA-61 in a 75% relative humidity atmosphere. This is not a direct measure of the rate that water vapor will attack samples of LC in a sealed cell, which might be faster if water vapor migrates across (through) the sealant, and which might be slower if the entire width of the sealant has to be degraded first for the moisture to affect the LC. However, we expect that the 12 kcal/mole activation energy probably also pertains to the temperature dependence of the relative rates of moisture attack on the LC through this sealant.

3.4 Thermal Stability Studies on LC Materials and Cells

Accelerated tests were made on the thermal stability of the new LC mixtures with added redox dopants by heating the mixture in evacuated tubes at $100^\circ C$ for long periods of time. The results

are summarized in Table IV. Each doped LC became darker and more conductive after the $100^{\circ}C$ heating, but the dc-DS characteristics remained essentially the same (as noted by $V_{90\%S}$) and no crystals or solid products were formed. We have found that the redox-doped ester mixtures generally become more conductive on standing, as indicated in Table IV for the resistivity of unsealed HRL-26N35 and -26N36 samples stored in a desicator at $23^{\circ}C$.

The thermal storage stability of redox-doped LCs at elevated temperature in sealed cells was studied by examining the effects of more than 3000h of storage at $80^{\circ}C$, as shown in Table V. The cells were pre-sealed with Norland NOA-61 optical cement around the perimeter spacer, were backfilled with LC after evacuation, and the filling hole was plugged with In and covered with the Norland NOA-61. The periods of heating, which totaled 3019h, caused no significant visual effects of degradation, i.e., no surface misalignment, no crystals, and no precipitates. This long period of $80^{\circ}C$ storage of HRL-26N25 and -26N36 in the sealed cells caused little resistivity change. The dc-DS characteristics of two cells were not changed significantly by the heated storage, but in a third cell the higher voltage (16.1 V) required for 90%S indicates that some degradation occurred in this HRL-26N36 mixture--possibly the introduction of some ionic impurities with a lower conductivity anisotropy than the redox dopants.

TABLE IV. Thermal Stability of Redox-Doped LC in Evacuated Tubes at 100°C.

Conditions and Measurements[a]	HRL Mixtures and Results[b]			
	26N4	26N25	26N35	26N36
Resistivity (ohm-cm), $10^{-9}\rho$				
-Initial	2.5	2.7	7.1	8.9
-After 1173h at 23°C, in cell[c]	---	---	3.4	2.8
-After 100°C in evacuated tube	0.5	2.3	1.5	1.0
Heating time: 100°C, evac. tubes	2300h	837h	1173h	1173h
Visual color change from heating	darker	darker	darker	darker
dc Voltage required for 90% S				
-Initial	---	---	13.6V	11.9V
-After 100°C in evacuated tube	---	---	13.3V	11.7V

[a] Measurements made at 23°C in float glass/ITO/PVA cells with 25 μm spacers.

[b] Each LC doped with 0.5% each of dialkylferrocene (DBF or DHF) and TFM.

[c] Unsealed cell stored in desiccator.

TABLE V. Effects of 80°C Storage on Redox-Doped LCs in Sealed Cells.

Conditions and Measurements	HRL Mixtures and Results	
	26N25	26N36
Heated Storage time at 80°C	3019h	3019h
Resistivity (ohm-cm), $10^{-9}\rho$		
-Initial	5.0, 3.2	6.1, 7.6
-After heating	4.6, 4.6	4.7, 7.6
dc Voltage for 90% S		
-Initial	--, 14.8V	13.0, 14.6V
-After heating	--, 15.5V	16.1, 13.9V

[a] Measurements at 23°C in cells of float glass/ITO/PVA with 12.7 μm Mylar spacers, sealed with Norland NOA-61.

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Low temperature storage effects on sealed cells of redox-doped HRL-26N25 and -26N36 were also examined, as indicated in Table VI. These cells showed no alignment changes or other ill effects from storage in the -60° to -20°C range, even though these temperatures are below their eutectic melting points. The changes in resistivity and in $V_{90\%S}$ are relatively small, indicating that the dopants remained in solution during the low temperature storage.

The electrochemical stability (i.e., dc-DS lifetime) of the redox-doped mixtures in sealed cells was studied at 55°C with 20 V dc applied continuously. The results of these experiments are summarized in Table VII and in Figure 10. The end of life of each cell was taken as the first observable defect, which was usually a brown deposit near the filling hole or along one edge of the perimeter seal. Most of the cells had lifetimes much longer than those we had found previously[1] using Ablefilm 539-Type II as the sealant for cells with other ester LCs at 55°C. The four best cells had lifetimes of 2312, 3091, 5279 and 6053h, which are all much longer than the lifetimes of unsealed cells studied previously.[1] This shows that these new LCs are capable of long operational lifetimes at elevated temperatures in well sealed cells. All of the cells in Table VII with short lifetime of <100h were sealed poorly and leaked. One-half of the cells with <100h lifetime had brown deposits next to the filling hole, where the LC might have had some contact

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TABLE VI.   Effects of Low Temperature Storage on
Redox-Doped LCs In Sealed Cells

Mixture	Storage Temp. °C	Days of Storage[a]	Measurements After Storage[b] $10^{-9}\rho$(ohm-cm)	V for 90%S
HRL-26N25	23	(Initial)	3.4	---
	-60	12	3.7	---
	-40	7	3.7	---
	-20	7	3.5	---
HRL-26N36	23	(Initial)	7.4	13.0
	-60	7	6.6	13.0
	-40	33	4.8	12.9
	-20	31	4.2	12.5

[a]Sequential storage times

[b]Measurements at 23°C in cells of float glass/ITO/PVA with
12.7 μm Mylar spacers, sealed with Norland NOA-61.

TABLE VII.   Sealant Quality Effects on Electrochemical
Stability of Redox-Doped LCs at 55°C.

HRL Mixture[a]	No. Cells[b]	Distribution of Cell dc lifetimes[c]				Longest Life
		<100h	<1000h	<5000h	>5000h	
26N25	12	5	4	2	1	5279h
26N35	2	1	--	--	1	6053h
26N36	4	--	4	--	--	789h

[a]Doped with redox pairs.
[b]Cells of float glass/ITO/PVA with 12.7 μm
Mylar spacers, sealed with Norland NOA-61.
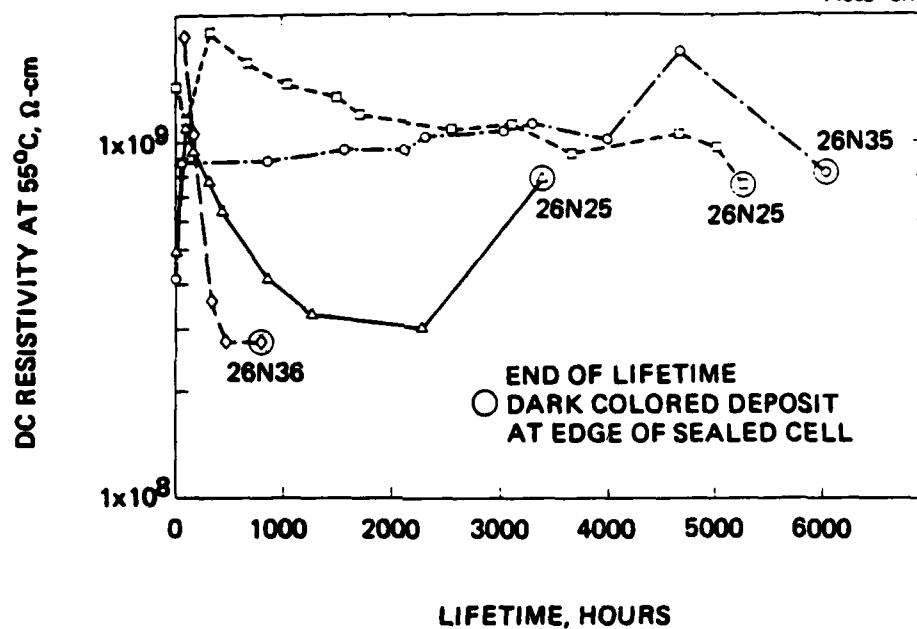[c]Lifetimes with 20 Vdc at 55°C.

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FIGURE 10   Sealant cell lifetime studies of
dc-DS at 55°C.

with the uncured sealant that was placed over the
indium plug and UV-cured. (On extended periods of
dc-DS at 55°C the brown deposits became metallic
looking deposits on the negative electrode, and
were identified as iron by Auger analysis.) Other
tests (55°C and 20 V dc) with redox-doped
HRL-26N25 in unsealed cells (Mylar perimeter
spacer only) showed a very short lifetime (<16h)
in the presence of a small drop of the uncured
sealant, a longer life (412h) in the presence of a
drop of UV-cured sealant, and a long life (3400h)
in the absence of any sealant. We believe that
the shorter lifetimes in Table VII are due to

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impurities from incompletely cured sealant, whose
electrochemical degradation effects appear to be
accelerated by the leakage of air into the cells.
Because there is a commonality of components in
these three LC mixtures, the differences in the
55°C dc-DS lifetimes which are shown in Figure 10
are believed to be due to the quality of the seal
rather than to differences in the purity of the
different LC mixtures.

4. CONCLUSIONS

1. Of three new LC ester eutectic mixtures with
lower viscosity which were formulated for DS
applications, HRL-26N36 is superior to HRL-26N25
and -26N35 in the width of its nematic range (-13°
to 78°C, undoped) and in its scattering level for
dc-DS with redox dopants added.

2. Thinner cells show faster dc-DS response times
than thicker cells, although with less change than
the usual square of thickness relationship.
However, thin cells show decreased scattering
levels at high temperatures and high voltages
(e.g.,> 50°C and >15 V). This may be due to space
charge build up at the PVA-coated electrodes
caused by the higher current levels.

3. At elevated temperatures the %S vs voltage
peaks at intermediate voltages (e.g., 10 to 12 V),

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and the ratio of decay-time/on-time increases.
These effects and the fast on-times at the higher
temperatures could compensate for a shorter length
pulse, such as might occur in a MOSFET matrix
display if the charge on the pixel capacitor leaks
appreciably during a frame time due to the higher
conductivity of the LC at high temperatures.

4.   An optical cement, Norland NOA-61, was found
to be superior to many other sealants (especially
epoxy types) in its thermal stability with ester
LCs at elevated temperatures. Well sealed cells
showed that long term dc-DS stability is possible
at elevated temperatures (e.g., >6000h at 55°C and
20 V dc). However, the lack of reproducibility in
fabricating well sealed cells was found to be the
limiting factor in the yield of long live dc-DS
test cells.

5.   The new mixtures with redox dopants show
favorable long term storage stability in sealed
cells between low and high temperatures of -60° to
80°C.

5.   ACKNOWLEDGMENTS

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